ESTABLISHMENT OF A SUPERCRITICAL PILOT PLANT AND THE HYDRODYNAMICS OF SUPERCRITICAL COUNTERCURRENT COLUMNS

by

Hendrik Hermanus Franken

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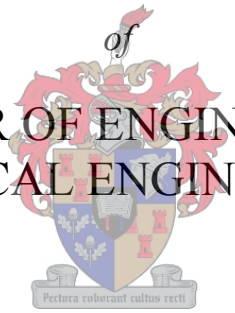
of the requirements for the Degree

of

MASTER OF ENGINEERING
(CHEMICAL ENGINEERING)



in the Faculty of Engineering
at Stellenbosch University

Supervisor
C.E. Schwarz

Co-Supervisor
J.H. Knoetze

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Declaration

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Abstract

Supercritical fluids are enjoying ever increasing popularity as a solvent medium for extraction, stripping and absorption processes. Being readily tuneable and able to achieve sharp, highly efficient separations, supercritical fluids present an attractive alternative to traditional solvents, while using less intrinsically harmful compounds. Although the potential of supercritical fluids as solvents have been known for more than a century, there are still several areas of uncertainty, one being the hydrodynamics of extraction columns operating under supercritical conditions. This shortcoming can be attributed to the satisfactory performance of modified standard hydrodynamics to approximate column design, along with a predominant culture of overdesign in process engineering. Even though modified subcritical hydrodynamic models provide a good approximation they do not successfully predict the effect of changes in density, viscosity and surface tension of a supercritical fluid, leading to inaccuracies in column design.

This study investigates the state of hydrodynamics under supercritical conditions in counter current packed columns discussed in literature, identifies shortcomings in existing literature and devises a way of addressing the said shortcomings. **The primary objective of this study is to establish a multipurpose supercritical pilot plant capable of measuring hydrodynamics under supercritical conditions, followed by the secondary objective of measuring preliminary hydrodynamic data to prove the plant can deliver on its design requirements in measuring reliable hydrodynamic data.**

During a survey of available literature it was found that very little experimental work has been performed on hydrodynamics under supercritical conditions and especially on random packings. Further it is found that the systems investigated in literature were conducted under conditions of significant mass transfer. As mass transfer directly affects flow rates and fluid properties of the fluids in the column, it is vital to use systems with very little to no mass transfer. This ensures the most accurate approach possible when investigating fundamental hydrodynamic behaviour. Finally it was found that there are no well-defined correlations available for a wide range of packings, fluid properties and hydrodynamic phenomena for columns under supercritical conditions.

To remedy the shortcomings in hydrodynamic data it was decided that more pilot plant work is required. It was found that no pilot plants available can measure hydrodynamic data. An investigation was performed into retrofitting available pilot plants, plants used by other research groups and commercially available plants. It was concluded that the best option was

to salvage the major parts of an existing old pilot plant and use them to construct a new, customized pilot plant. This provides the opportunity of constructing a custom, multipurpose pilot plant capable of use in future research.

After an initial concept design a full design of the new pilot plant was performed. The plant consists of two columns of 17 mm and 38 mm inside diameter and 3.5 m and 1.5 m packed height, respectively, and is capable of pressures and temperatures of up to 300 bar and 200°C. Furthermore the pilot plant can measure liquid hold-up, pressure drop, flooding and entrainment in accordance with the objective of measuring supercritical hydrodynamic data. Liquid hold-up was determined by stopping the process and allowing the column to drain, after which the volume drained was measured. To measure the pressure drop an Endress+Hauser Deltabar S PMD75 DP cell was used. Flooding was determined using the measured pressure drop and volumetric rate of column overheads, from where a hydrodynamically inoperable state is defined. Overall entrainment, although unlikely due to the presence of a demister in the column, was investigated by comparing the column overheads to literature phase equilibria.

Preliminary hydrodynamic testing was performed using the 38mm diameter column packed with 1/4" Dixon rings. Testing is performed with at 120 bar and 40°C with a CO_2 supercritical phase and polyethylene glycol liquid phase with an average molar mass of 400 (PEG 400). The hydrodynamic data gathered showed expected trends, but showed discrepancy with literature due to differences in liquids used, column packing and experimental system between the respective studies.

Keywords: Carbon Dioxide, Countercurrent, Flooding, Liquid Hold-up, Hydrodynamics, Pilot Plant, Pressure Drop, Supercritical.

Uittreksel

Superkritiese vloeistowwe is besig om toenemende gewildheid as 'n oplosmiddel vir ekstraksie, stroping en absorpsie prosesse te geniet. Hierdie gewildheid is as gevolg van ŉ vermoë om skerp, hoogs effektiewe skeidings te bewerkstellig deur gebruik te maak van ŉ maklik aanpasbare oplosmiddel wat minder intrinsiek skadelik is as tradisionele oplosmiddels. Hierdie voordele lei daartoe dat superkritiese vloeiers as ŉ aantreklike alternatief tot tradisionele oplosmiddels gesien kan word. Alhoewel die potensiaal van superkritiese vloeistowwe as oplosmiddels al vir meer as ŉ eeu bekend is, is nog weinig eksperimentele werk al gedoen oor die hidrodinamiese gedrag van superkritiese gepakte kolomme. Hierdie tekortkoming kan toegeskryf word tot die bevredigende prestasie van aangepaste standaard hidrodinamiese korrelasies gedurende superkritiese kolomontwerp en ŉ oorheersende kultuur van oorontwerp in proses-ingenieurswese. Alhoewel aangepaste standaard hidrodinamiese korrelasies ŉ aanvaarbare benadering bied, beeld dit nie die effek van die veranderde digtheid, viskositeit en oppervlakspanning van ŉ superkritiese vloeistof uit nie, wat lei tot foute in kolomontwerp.

Hierdie studie ondersoek die stand van superkritiese hidrodinamika in literatuur, spesifiek in teenstroom gepakte kolomme. Tekortkominge in die bestaande literatuur is geïdentifiseer en 'n metode om die genoemde tekortkominge reg te stel is bedink**. Die primêre doel van hierdie studie is om 'n veeldoelige superkritiese loodsaanleg te bou wat tot staat is om superkritiese hidrodinamika te meet, gevolg deur die sekondêre doelwit wat die meet van voorlopige hidrodinamiese data behels, wat sal bewys dat die loodsaanleg voldoen aan ontwerpsvereistes.**

Tydens 'n opname van beskikbare literatuur was daar gevind dat weinig eksperimentele werk al gedoen is in die veld van superkritiese hidrodinamika, en nog minder oor sogenoemde ongeordende of 'random' kolompakkings. Verder is daar gevind dat eksperimente uitgevoer in literatuur slegs bestaan uit stelsels waar beduidende massa-oordrag plaasvind. Aangesien massa-oordrag die vloeitempo en fisiese eienskappe van die vloeiers in ŉ kolom direk beïnvloed, is dit noodsaaklik om gebruik te maak van stelsels met baie min of geen massa-oordrag. Dit verseker ŉ akkurate benadering tot die meet van fundamentele hidrodinamiese gedrag. Laastens is gevind dat daar geen hidrodinamiese korrelasies beskikbaar is wat ŉ wye verskeidenheid van kolompakkings, vloeier eienskappe en hidrodinamiese verskynsels onder superkritiese toestande dek nie.

Om die tekortkominge in superkritiese hidrodinamika in literatuur aan te spreek, word meer eksperimentele loodsaanlegwerk vereis. Daar is gevind dat geen van die beskikbare loodsaanlegte hidrodinamiese data kan meet nie. Ondersoek is ingestel tot die ombouing van bestaande loodsaanlegte, aanlegte wat gebruik is deur ander navorsingsgroepe en kommersieel beskikbare aanlegte. Daar is tot die gevolgtrekking gekom dat die beste opsie is om 'n nuwe loodsaanleg self te bou en gebruik te maak van parte uit een van die ou bestaande aanlegte om kostes laag te hou. Sodoende kan 'n veeldoelige, pasgemaakte loodsaanleg gebou word wat ook vir toekomstige navorsing gebruik kan word.

Na 'n aanvanklike konsep ontwerp vir die nuwe loodsaanleg, is 'n volledige ontwerp gedoen. Die aanleg bestaan uit twee kolomme van onderskeidelik 17 mm en 38 mm binnedeursnee en 3,5 m en 1,5 m gepakte hoogte, en is in staat om eksperimente by 'n maksimum druk en temperatuur van tot 300 bar en 200°C uit te voer. Verder is die loodsaanleg in staat daartoe hidrodinamiese data te meet, naamlik die vloeistofophoud in die kolom, drukval oor die kolompakking, kolomvloed en druppel meesleuring. Die vloeistofophoud in die kolom is bepaal deur alle voer tot die kolom te stop en tyd toe te laat vir die vloeistof om te dreineer, waarna die gedreineerde afgetap en gemeet is. Om die drukval te meet word 'n Endress+Hauser Deltabar S PMD75 DP sel gebruik. Kolomvloed is bepaal met behulp van die drukval oor die kolom en die vloeitempo van die kolom se boonste produkstroom, van waar 'n hidrodinamies onbruikbare toestand gedefinieer word. Algehele druppel meesleuring, alhoewel onwaarskynlik as gevolg van die teenwoordigheid 'n ontwasemer in die kolom, is wel ondersoek deur die vloeistofinhoud in die kolom se boonste produkstroom te vergelyk met fase ewewigsdata in literatuur.

Voorlopige hidrodinamiese eksperimente is uitgevoer met behulp van die 38mm deursnee kolom gepak met 1/4 " Dixon ringe. Eksperimente is uitgevoer by 120 bar en 40 ° C met 'n CO_2 kritiese fase en 'n poliëtileenglikol vloeistof fase met 'n gemiddelde molêre massa van 400 (PEG 400). Die hidrodinamiese data het verwagte tendense getoon, maar diskrepansies met literatuur waardes. Die verskille tussen die eksperimentele en literatuur data word geregverdig deur die verskille tussen die vloeistowwe, pakking en eksperimentele stelsels wat in die onderskeie studies gebruik is.

Sleutelwoorde: Drukval, Hidrodinamika, Kolomvloed, Koolstofdioksied, Loodsaanleg, Superkritiese, Teenvloei, Vloeistofophoud.

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To the one true God: Father, Son and Spirit. Thank you for creating a world full of wonders, and giving me the strength, curiosity and intelligence to explore it.

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Nomenclature

Symbol	Description	Units
a	Packing surface area per unit volume	m^2/m^3
d	Column/Packing diameter	m
d_p	Particle/Sphere diameter	m
$\in$	Fractional void volume	m^3/m^3
F_G	Gas capacity factor/Vapor flow factor	$(m/s).(kg/m^3)^{0.5}$
g	Gravity	m/s^2
G	Gaseous phase superficial mass flow rate	$kg/m^2.s$
H	Total packed height	m
h_L	Total liquid hold-up	m^3/m^3
h_{Ld}	Dynamic liquid hold-up	m^3/m^3
$h_{Ld,0}$	Dynamic liquid hold-up below the loading point	m^3/m^3
h_{Ls}	Static liquid hold-up	m^3/m^3
K_x	Equation constant of number x	–
L	Liquid phase superficial mass flow rate	$kg/m^2.s$
n_t/H	Separation Efficiency/Number of theoretical stages per 1 m packing height	m^{-1}
$Ø_I$	Internal Diameter	mm
ΔP	Total measured pressure drop	Pa
$\Delta P/H$	Pressure drop per 1 m of irrigated or wet packing	Pa/m
$\Delta P_0/H$	Pressure drop per 1 m of dry packing	Pa/m
P	Pressure	Pa, bar
u_L	Liquid phase superficial velocity	m/s
u_G	Gaseous phase superficial velocity	m/s

Greek Symbols	Description	Units
δ	Liquid film thickness	mm
μ_L	Dynamic liquid phase viscosity	Pa.s
μ_G	Dynamic gaseous phase viscosity	Pa.s
Φ	Flow parameter	-
$\Delta\rho$	Density difference (liquid minus gaseous)	kg/m^3
ρ_G	Gaseous density	kg/m^3
ρ_L	Liquid density	kg/m^3
σ	Liquid surface tension	mN/m
Dimensionless Numbers	**Description**	
Bo	Bond Number	
Fr_L	Froude Number of liquid	
Re_G	Reynolds number of the gaseous phase	
Re_L	Reynolds number of the liquid phase	
ψ	Ergun friction factor	
ψ_{VL}	Total resistance coefficient	
Abbreviations and Acronyms	**Description**	**First mentioned in section**
DP Cell	Differential Pressure Cell	4.1.6
GUI	Graphical User Interface	4.2.5
HMI	Human Machine Interface	4.2.5
Mw	Molar weight (in g/mole)	4.2.6
PLC	Programmable Logic Controller	4.2.5
PEG	Polyethylene glycol	4.2.6
PPG	Polypropylene glycol	4.2.6
PTHF	Polytetrahydrofuran	4.2.6

1. Introduction

The packed column is at the heart of many industrial processes in the role of absorber, stripper and rectification column. Since initial research interest into column design in the 1930s, significant improvements and changes have occurred in the field. The range of applications has increased and packing technology has developed to meet ever higher efficiency needs. Even though columns are 'old' technology, it is by no means a mature technology and some areas are still poorly understood. One such area is the relatively new application of supercritical fluid fractionation and extraction.

Although the potential use of supercritical fluids as solvents have been known for more than a century, fractionation with supercritical fluids has seen little industrial application in packed columns. (This is due to several reasons, which will be discussed in Section 1.3). Recently industry interest has increased, leading to renewed research efforts in supercritical extraction in packed columns. Very little experimental work has been done on the hydrodynamics of these systems, which can be attributed to the satisfactory performance of modified standard hydrodynamics to approximate column design and the use of pilot plant studies. The use of subcritical hydrodynamics does, however, lead to costly column overdesign.

1.1 Hydrodynamics

Hydrodynamics in countercurrent columns entail the study of the behaviour of two discrete phases flowing over column internals. A denser phase is added at the top of the column, from where it flows over the surface of the column internals with the help of gravity. A second, less dense phase is actively pumped into the bottom of the column and flows upwards through the spaces between internals. While flowing through the column in opposite directions the phases interact, typically effecting mass transfer. The interaction between the phases, and the column internals, causes the hold-up of the denser phase in the column and a pressure drop over the column internals. These are two phenomena central to the study of column hydrodynamics. (1)

The importance of hydrodynamics comes to light when sizing and designing new columns or retrofitting old columns, where the operation of the column is determined by hydrodynamic capacity (1). The hydrodynamic capacity is defined as the combination of vapour and liquid rates at which the column becomes hydrodynamically inoperable or where performance, typically mass transfer performance, becomes unacceptable (2; 3). The capacity is directly dependent on the physical aspects that limit flow in the column, being the column internal

properties, the diameter of the column, as well as the properties of the two co-existing phases (4).

Hydrodynamics in columns operated at atmospheric pressure are well developed, using proven correlations and dimensionless numbers to predict and describe both the gas and liquid phase flows, and the interaction between phases (1). In contrast to this, little work has been done on hydrodynamics under supercritical conditions, with limited research stating and confirming the use of modified standard correlations. To date modified subcritical hydrodynamics have been used with satisfactory application to approximate column design (5). Even though modified subcritical hydrodynamics provide a good approximation of such systems, they do not successfully depict the higher density, viscosity and surface tension of a supercritical fluid. This leads to inaccuracies in column design. A detailed discussion of hydrodynamics under supercritical conditions is presented in Section 2.3.

1.2 Supercritical Fluids

A supercritical fluid is any substance in a state above its critical pressure and temperature. The substance is neither in a liquid nor a gaseous phase, but rather in a single intermediate phase between the two extremes. Supercritical fluids have a number of attributes that make them ideal for use in industrial separations and extractions. (For a complete discussion, please see Section 2.1.)

The principles behind supercritical fluids have been known since the early 1800s (6), followed by the first paper identifying it as a solvent published in 1879 by Hannay and Hogarth (7). Since then numerous research papers have been published on the topic, but, in spite of this, the process has only recently received significant industry attention. This was due to an initial abundance of inexpensive energy and raw materials that negated the need for, what was at the time perceived to be, an expensive and dangerous process (8). This led to supercritical extraction being 'put on the shelf' for many years. Recently, the situation has started to reverse with increased competition for energy and raw materials, along with the ever present drive to refine industrial processes, leading to the demand for ever better separation and higher efficiency (9). The development of material sciences also made a contribution to this reversal, with materials able to withstand the high pressures becoming cheaper and more obtainable. Further, supercritical fluids have a few inherent advantages over traditional solvents (8), typically being much less harmful solvents than traditional organic solvents and able to effect difficult separations that are virtually inseparable by traditional means (10). This, and other advantages discussed in Section 2.1.2, has caused supercritical fluid extraction and separation to be revived as a possible alternative technology.

1.3 Supercritical Fluid Extraction

Supercritical fluid extraction can be described as the process of separating one or more components from a liquid mixture or solid matrix using supercritical fluids as the extracting solvent. Applying this definition, supercritical extraction can be considered as a sample preparation step for analytical purposes, to strip unwanted material from a product (e.g. decaffeination of coffee and tea) or to collect a desired product (e.g. essential oils) (11). In the case of a countercurrent column the supercritical fluid phase takes the place of the conventional gas phase and is used to strip a specific component or range of components out of the liquid phase. This provides a close analogy with standard stripping and rectification columns. (12)

Supercritical extraction has advantages over classical extraction, with rapid mass transfer due to the low viscosities and high diffusivities associated with supercritical fluids. Furthermore the extraction can be made selective by controlling the system temperature and pressure, which in turn affects the supercritical phase's properties. Recovery is often simple, with a reduction in pressure to a point below the critical pressure of the solvent causing the supercritical fluid to revert to a gas and the dissolved solutes to precipitate. This leaves little to no solvent residues in the product. The most commonly used supercritical fluid solvent is carbon dioxide, or CO_2, occasionally modified by co-solvents such as ethanol or methanol. CO_2 is a popular green solvent for a wide range of chemical and biochemical processes, being non-toxic and cheap with relatively mild operating conditions. (8)

1.4 Pilot Plants

Traditionally, pilot plant data are used for verification and optimisation of simulated data. This refined data is then used to provide a better final design solution for industry scale operations. In supercritical fluid extraction the complex phase behaviour, along with the lack of well-established design methods, hinders the simulation of supercritical extraction solutions. This leads to pilot plants being used as the primary source of design data for industry solutions. (8)

Due to the significant investments required to construct pilot plants for research, plants are typically designed to cater for a multitude of different applications within the overarching technology, maximising the possible investigations and research outputs. The average research pilot plant will have a much higher degree of flexibility than an industrial plant designed for a specific application. This constitutes the development of multi-purpose research pilot plants, capable of delivering experimental data over a wide range of applications.

1.5 Aims, Objectives and Scope

As mentioned in Section 1.1, very little work has been done on the characterization of hydrodynamics under supercritical conditions (13; 14), and subsequently on supercritical design philosophies. The ultimate aim would be to provide a better design basis for supercritical columns by establishing standard semi-empirical or empirical hydrodynamic models for random packed columns. This is, however, beyond the scope of this project. This work aims to provide the required groundwork for future work to fulfil this overarching aim.

In order to meet the requirements of this project within the overarching aim, the following specific aims are identified for this project:

- Establish a pilot plant capable of measuring hydrodynamics under supercritical conditions.
- Prove the pilot plant works and is capable of delivering reliable hydrodynamic data.

To fulfil the first aim currently available facilities, pilot plants discussed in literature and commercially available pilot plants are to be investigated. It is found that building a new pilot plant in-house provides the best option, providing that an existing pilot plant is deconstructed and its components salvaged for reuse in the new pilot plant. The new pilot plant is to be designed according to specifications and limitations inherited from the old pilot plant, along with general safety and modernization concerns. To further exploit the opportunity of building a new pilot plant, the design is to be as versatile and adaptable as possible to allow for future investigations in countercurrent extraction and fractionation and solid extraction. The exact, expanded design objectives can be found in Section 3.2.1 and the pilot plant scope and limitations in Section 3.3.1.

To achieve the second aim the pilot plant is used to measure hydrodynamic data. The measurement of hydrodynamic data concerns the pressure drop, flooding, liquid hold-up and, if possible, entrainment over a packed column. An initial fluid system for testing is identified and an experimental procedure established, followed by the collection of data. This data will be compared with currently accepted correlations and literature data. The exact, expanded, experimental objectives can be found in Section 3.2.2 and the experimental scope and limitations in Section 3.3.2.

A subsequent study will use the established pilot plant to gather the required hydrodynamic data to establish a supercritical hydrodynamic model and ultimately meet the overarching goal of this research.

1.6 Thesis Structure and Mind Map

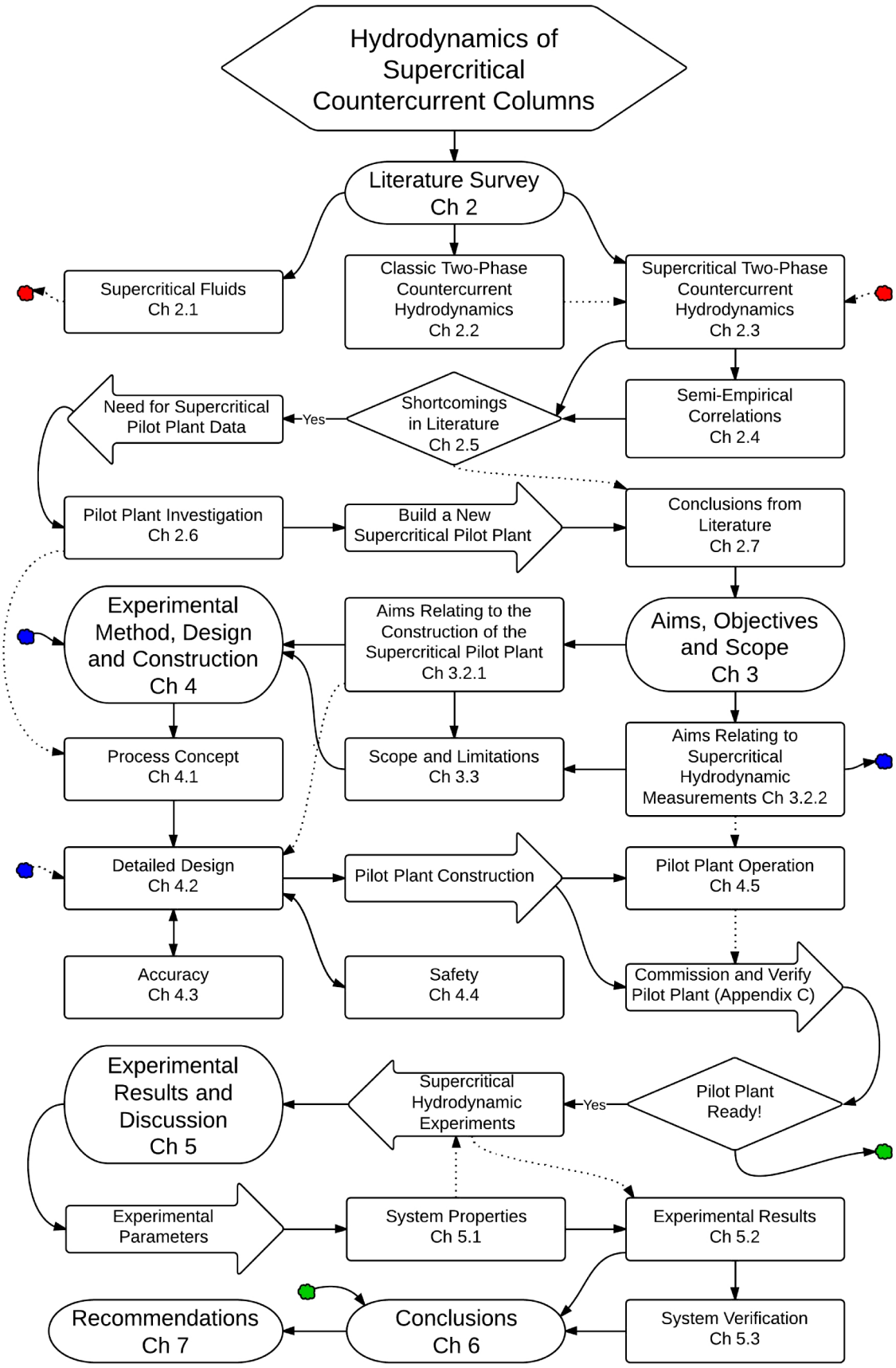

Figure 1- 1: Thesis mind map.

2. Literature Review

The literature review section contains an introduction to the key concepts in supercritical fluids and classic two-phase countercurrent hydrodynamics. This is followed by a full investigation into currently available supercritical two-phase countercurrent hydrodynamic literature and correlations. After identifying shortcomings in literature, it is noted that additional pilot plant data can be used to fill the gaps in literature. Pilot plant options are investigated, followed by a summary of the overall conclusions from the literature review.

2.1 Supercritical Fluids

2.1.1 Definition and Properties

A supercritical fluid is defined as any substance in a state above its critical temperature and pressure. This state follows the rules of neither a gas, nor a liquid, but rather a new set of properties describing an intermediate phase of matter. This phase has attributes somewhere between that of a liquid and a gas, for example being able to effuse through solids like a gas, and dissolve materials like a liquid. As this combination of properties is sometimes hard to picture for someone new to the phenomenon, the behaviour of a substance in the supercritical phase is best described as that of a very mobile liquid. Supercritical fluids possess a number of attributes that make them ideal for use in industrial separations and extractions (8). These attributes are dependent on the substance's temperature and pressure relative to its critical point.

Critical Point and Detailed Phase Definition

The critical point of a pure compound lies at the end of the gas-liquid equilibrium curve and defines the critical temperature and pressure. Hence the point indicates the very start of the boundaries of the supercritical phase. All temperature and pressure states beyond the critical point are in the supercritical phase, except at extremely high pressures where a solid phase may form (see Figure 2- 1). The mathematical definition of the critical point is where:

$$\left(\frac{\delta P}{\delta V}\right)_T = 0 \qquad [1]$$

and

$$\left(\frac{\delta P^2}{\delta V^2}\right)_T = 0 \qquad [2]$$

Interpreting Equations [1] and [2], it is seen that the compressibility of the material becomes infinite. It must be noted, however, that if one moves around the supercritical point and the mentioned boundaries, no visible changes are observed and the substance moves seamlessly from one phase to another. As a consequence, there is no clear physical delimitation of the supercritical phase, but rather a conventional implied boundary. Despite this the supercritical state is defined as a separate phase, as can be seen in Figure 2- 1 on the following page. In the figure it can clearly be seen that the supercritical fluid phase is separate from the classical states of matter, namely solids, liquids and gases.

There is no standard definition of the supercritical fluid phase of a pure compound and an attempt will be made to present a definition derived from basic principles in the following discussion. As mentioned earlier, the critical point is defined by a set critical temperature and pressure. The critical pressure of a substance is defined as being equal to its vapour pressure at its critical temperature. In turn the vapour pressure of a substance is defined as the pressure exerted by a vapour in thermodynamic equilibrium with its respective condensed phase in a closed system. Comparing these two definitions it can be deduced that in any state above the critical point, the force exerted by the implied vapour pressure is higher than the liquid's physical limits. That is, the pressure exerted by the 'vapour' exceeds the cohesive forces in the liquid and the clear interface between the phases break down. Explaining this from a liquid point of view, it can be reasoned that the repellent forces between molecules in the liquid start exceeding the attractive forces due to the high pressure forcing molecules together. (15)

This behaviour of supercritical fluids at the molecular scale gives rise to one of its fundamental features, being a localised clustering of molecules. This clustering, as most of the properties of supercritical fluids, also follows an intermediate path and occurs neither to the high extent witnessed in liquids and solids, nor that of gases where no significant clustering occur. Clustering in the supercritical phase is caused by weak intermolecular forces, such as Van der Waals forces, and is much more dynamic and weakly bound than in the bonds between molecules in liquids. This influences the solution structure, which in turn influences the transport properties of the fluid, producing the attributes that make supercritical fluids such effective solvents. (16; 17)

From this discussion the supercritical phase can be dually simplified as either a dense supersaturated vapour, being unable to condense due to the internal repellent forces, or a highly excited liquid which is unable to evaporate, due to high pressure. At first glance this may seem to be contradictory statements, but the reasoning is substantiated if one investigates the pressure and temperature dependence of various supercritical phase properties.

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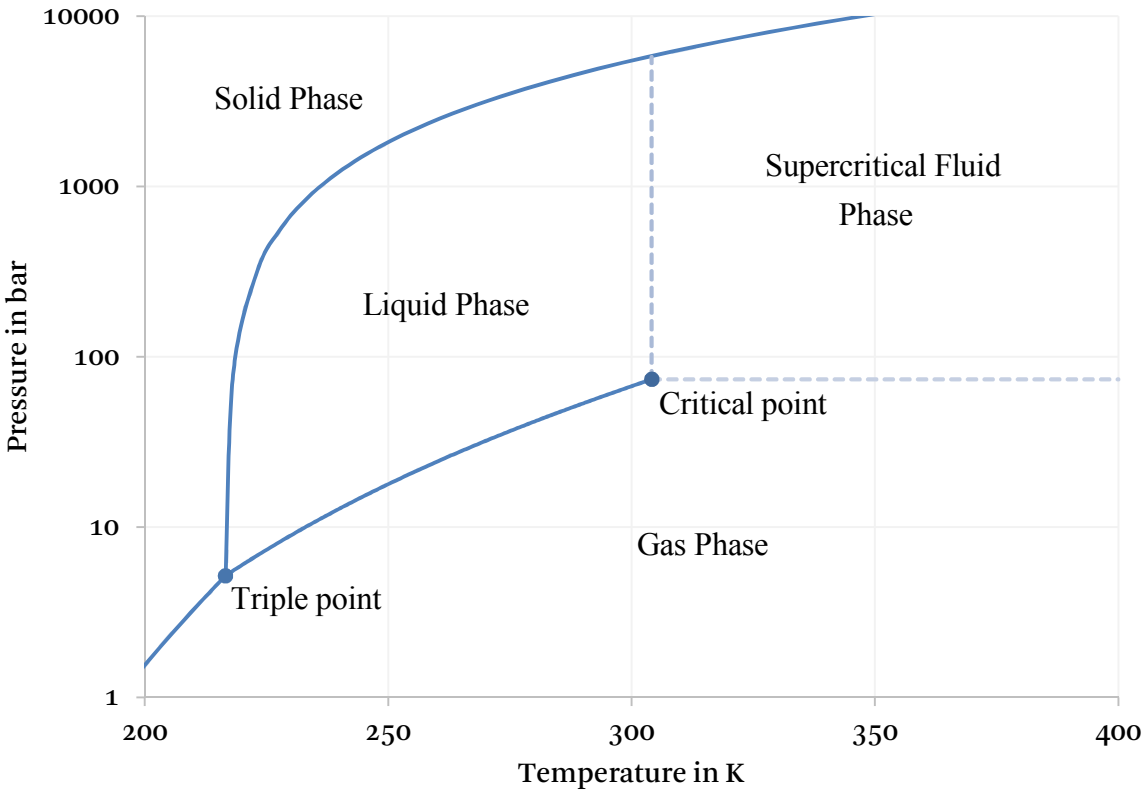


Figure 2- 1: CO_2 pressure-temperature phase diagram.
[Drawn from data calculated by NIST WebBook using the equation of state proposed by Span and Wagner (18)]

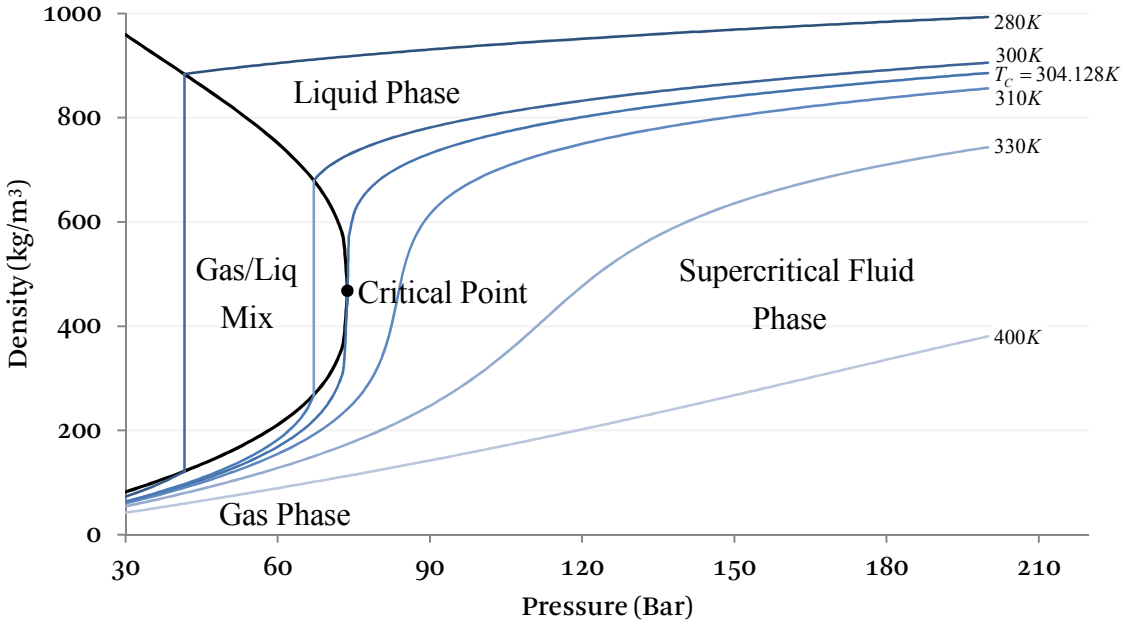


Figure 2- 2: CO_2 density-pressure phase diagram at varied temperatures.
[Drawn from data calculated by NIST WebBook using the equation of state proposed by Span and Wagner (18)]

Temperature and Pressure Dependence

According to Gibbs' phase rule (19), the properties of a single component, present in a single phase, can be defined using two intensive variables. The pressure and temperature of such a state represent the fundamental dependencies of a phase, with all subsequent terms derivable through thermodynamics. In order to define the dependence of the supercritical phase on each of these variables, one is kept constant while the other is varied.

At constant pressure, changes in temperature play a significant role in the supercritical phase. This is especially true close to the critical point where a slight isobaric change in temperature will cause disproportionally large changes in the density and viscosity of the fluid. This is confirmed when looking at the temperature dependence of the density in Figure 2- 2. An increase in temperature causes a decrease in density and viscosity, which corresponds with a more gas-like phase forming. As the density and viscosity directly influences the fluidic properties of the supercritical phase this is an important factor when investigating hydrodynamics.

At constant temperature, the density and viscosity dependence of a supercritical fluid is, just like the temperature dependence, directly related to the pressure. An increase in pressure leads to an increase in density and viscosity and a more liquid-like phase. Once again, close to the critical point, small changes in the pressure drastically affect the properties of the fluid, leading to rapid changes from gas-like to liquid-like behaviour and vice versa. This can be seen very well in Figure 2- 2 at the critical temperature, where the density will change significantly with a small increase or decrease in pressure.

General Properties

The general properties of a supercritical fluid are affected by its intermediate nature, the phenomenon of molecule clustering and its temperature and pressure dependence. The individual properties of a supercritical fluid may be summarised as follows (9):

The density of the phase can be gas-like or liquid-like, depending on the state relative to the critical point. The density usually tends more towards that of the corresponding liquid phase. As discussed in the temperature and pressure dependencies the density increases with a decrease in temperature and/or an increase in pressure.

The viscosity is of intermediate value, falling between that of the liquid and the gas. Viscosity increases with a decrease in temperature and/or an increase in pressure. In this aspect the supercritical phase is more liquid-like, with the temperature and pressure dependence being directly the inverse of that of a gas.

Thermal conductivity falls between the general values of the liquid and gaseous states of the compound. Thermal conductivity increases with a decrease in temperature and/or an increase in pressure. The temperature dependence corresponds with that of a liquid, but not with that of a gas.

Diffusivity also falls between that of the pure gas and liquid states, with values tending more towards a gas-like state. The diffusivity of supercritical fluids is in the order of up to five times larger than the liquid state. This contributes to higher effective mass transfer rates.

The surface tension of supercritical fluids is between that of the liquid and the gas, although values tends more towards that of the gas. It is an important variable when considering wetting in packed columns, where a low surface tension is preferred. The surface tension decreases as the pressure increases, and has a complex relationship with temperature.

From the above discussion of the properties it is seen that the previous assumption that the supercritical phase is an intermediate between the liquid and gas phases, can be affirmed. All the properties discussed, lie between that of the liquid and gas states, with some tending more towards one or the other. This mixture of properties leads to supercritical fluids being advantageous solvents. To fully consider the merits of supercritical fluids as solvents, a more in depth comparison with traditional solvents is required.

2.1.2 Advantages and Disadvantages

In the prior discussion the supercritical phase, its relevant properties and their effects on its use as a solvent were addressed. To truly judge the viability of a supercritical fluid as a solvent, the advantages and disadvantages over traditional solvents, typically organic liquids, have to be considered. More specific to this study are the advantages and disadvantages of a supercritical and traditional solvents in a packed column.

Processes using packed columns operating with supercritical fluids hold a number of advantages over traditional gas-liquid columns. These include, but are not limited to, the following:

- Some supercritical solvents can be operated at low temperatures and even close to ambient temperatures, avoiding thermal degradation of labile components and high heating costs.
- Supercritical fluids are very flexible solvents with a wide range of separations achievable with variation in temperature and pressure. The operating conditions of a column can be fine-tuned to exactly meet the needs of a specific separation or changed during operation to compensate for an irregular feedstock.

- Supercritical fluids can exhibit a high degree of selectivity and can even distinguish between different molecules according to its chain length (20) and functional group (21). This selectivity allows for more efficient processes and sharper separations.
- The properties of a supercritical solvent as discussed in Section 2.1.1 generally allows for higher mass transfer rates than possible in traditional solvents.
- The extracted solute is easily recovered and the process leaves little to no residual solvent in the product.
- The solvent is readily recyclable with no significant theoretical losses. Therefore the process requires very little addition of fresh solvent during operation.
- Supercritical fluids are ordinarily less toxic and more environmentally friendly than equivalent traditional solvents.

No process is without its disadvantages and supercritical fluid processing is no exception. Some disadvantages are:

- Supercritical processes operate at much higher pressures than traditional separations. This implies higher process equipment specification requirements and stricter safety and maintenance procedures.
- The technology is still immature, with well established, standardised design methods and operating philosophies few and far between.
- Supercritical phase behaviour is complex because of the non-ideality and intrinsic asymmetric nature of the system.
- Is not easily modelled in commercially available process simulators.

The advantages and disadvantages discussed are summarized from literature (8; 22) and the discussion in Section 2.1.1, unless otherwise referenced.

Although it might seem that the advantages outweigh the disadvantages, one of the pivotal points that has not been discussed yet is the economic viability of supercritical fluid extraction. As supercritical fluid extraction is still a relatively fledgling technology, very little broad scope economic analysis has been done and no definite consensus has been reached (8).

2.1.3 Economic Considerations

The general impression in industry is that initial costs for supercritical technologies are excessively high because of the high pressure equipment requirements, leading to a more expensive option when compared to traditional solvents (23; 22). While there is no conclusive study showing this to be true or false for the technology as a whole, some studies have shown promise in certain niche areas.

Firstly, it has been shown that supercritical fluid extraction requires marginally lower energy input (24; 25; 26), which leads to lower operating costs. Secondly, Perrut (23) has shown that the price of a supercritical extraction facility scales well with increasing capacity. Thirdly, a review by Pereira and Meireles (27) showed that when estimating factory costs using the Cost of Manufacturing-method as defined by Turton, et al. (28), supercritical fluid extraction is significantly less expensive in operating cost. A host of smaller economic evaluations for niche applications have been done with relative success in showing supercritical fluids to be economically feasible and a viable alternative to traditional methods (29; 30; 31; 32; 33).

Unfortunately, until a fully comprehensive study has been done with regard to economic viability, it remains uncertain if supercritical fluids can be assumed to provide a better option in general and case-by-case investigations are recommended. Despite this supercritical fluid extraction processes have been proven a viable option and is used commonly in industry in several commercial niche areas.

2.1.4 Commercial Supercritical Extraction

The potential of supercritical fluids as effective and efficient solvents has been known for more than a century, although application in industry has only truly taken root since the 1980s. This is attributed to a former relative abundance of energy and raw materials, causing little need for highly effective separations (8). Further, high pressure applications were typically avoided as a misconception of the costs involved was commonplace. According to Nieuwoudt (9), rising energy costs and stricter environmental legislations has forced industry to reconsider supercritical separation. This, along with increasing consumer based demand for higher quality and purity products, presents supercritical fluids as an appealing alternative extraction technology.

Indeed supercritical fluid extraction can sometimes provide a solution where other methods such as distillation, absorption, membranes and liquid- liquid extraction are impractical or impossible (10). Further supercritical fluids have a few inherent advantages over traditional solvents (8), importantly being much less harmful solvents than traditional organic solvents. Processing by some supercritical solvents, such as CO_2, can even allow for a product to be certified as 'Organic', as long as it meets other production and processing specifications (34). This could allow for a product to enter an elite certification, eliciting higher market values.

Supercritical fluid extraction technologies have become commonplace in several niche markets, such as the food and beverage industry and the production of essential oils, pharmaceuticals and polymers. An important contribution causing widespread industrial use is that of Zosel (35), who developed and patented a method of extracting caffeine from green

coffee with supercritical CO_2. Further supercritical extraction techniques and applications in industry are covered in works such as those by McHugh and Krukonis (12), Kiran, Debenedetti and Peters (11) and Brunner (36).

Plants currently using supercritical technologies are not overly abundant, but do exist with applications mainly in the processing of natural products and foodstuffs. Of these the majority are located in Europe and the USA. Some examples are:

- The Kraft General Foods coffee decaffeination plant in Houston, Texas, with a capacity of 23 000 ton/a,
- The Lipton tea decaffeination plant in Germany with a capacity of 6 800 ton/a,
- The Flavex extraction plant for natural oils, capacity 300 ton/a (37), also in Germany.

A well-known provider of industrial supercritical solutions, Natex, cites some industrial batch plants that have been provided by them as follows (38):

- 1 200 ℓ plant and herb extraction plant - India,
- 1 700 ℓ hops and nutraceutical plant - New Zealand,
- 11 600 ℓ rice treatment plant - Taiwan,
- 51 000 ℓ wood impregnation plant - Denmark,
- 7 600 ℓ edible oil extraction plant - South Korea,
- 24 900 ℓ cork purification plant - Spain.

Supercritical fluid extraction is therefore a well-established technology in certain niche markets and proven as an industry scale solvent.

The commercial viability of supercritical columns in packed columns has been shown in several pilot plant studies for novel applications (9; 22; 37). This shows that the technology has as of yet undiscovered and unconfirmed applications that are viable for industrial scale application. It should however be noted that supercritical fluid extraction does not always provide the best solution (39; 40) and should not necessarily be the first choice of technology (41; 42).

2.2 Classic Two-Phase Countercurrent Hydrodynamics

2.2.1 Introduction

Hydrodynamics is defined by the Oxford dictionary as: "The branch of science concerned with forces acting on or exerted by fluids" (43) and is a sub-category of Fluid Mechanics. In a typical packed column two discrete fluid phases are flowing in opposite directions. As would be expected from the dictionary definition, these two fluids interact with each other and the column/packing geometry. This interaction determines the hydrodynamic capacity, which determines the design diameter of a column. The hydrodynamic capacity is the range of operability of a column and encompasses, among others, the pressure drop over the column, liquid hold-up in the column and flow rates of the respective fluids which is a function of the fluid properties and column internals. (1; 4; 44)

2.2.2 Packed Columns

The primary goal of a column and its internals is to promote the contact between two phases to achieve mass transfer. Mass transfer is affected by the contact between phases and can be maximized using certain column internals to best exploit the fluid properties and operational parameters. A supercritical extraction is analogous to a stripping or rectification column, where random and structured packings are typically the internal of choice.

Random packing was developed as an alternative to tray columns (1), providing a reduction in pressure drop, increase in capacity and reduced liquid hold-up. Random packing consists of a multitude of discrete units of a specific geometry packed into a column. This creates a randomized bed with a large surface area. The specific traits of a certain packing depends on the geometry of the individual units.

Structured packing followed random packing, providing a more consistent and predictable solution. Structured packing consists of crimped layers of wire mesh, corrugated or metal gauze sheets. The sheets form a distinctive pattern, usually consisting of triangular or sinusoidal channels arranged in parallel to each other and at an oblique angle relative to the column.

In structured packing liquid flows on the surface of the packing while gas flows upwards in the channels between packing elements. In this column setup both phases can be continuous. In a random packing, flow is difficult to predict as flow channels are arranged irregularly. Here both phases can be continuous through most of the column, although regions may exist where either is present as a discontinuous phase. (1)

In a column the liquid flow is the easiest to predict, as adhesion forces in the liquid will strive to maintain contact with column internals. This liquid flow is approximated as a falling film on the surface of column internals.

2.2.3 Falling Films

In columns the liquid phase flows as a film over the surface of the packing and the column wall. In both structured and random packing the lighter gaseous phase flows in an opposite direction, exerting a shear force on the falling film. This shear force works on the boundary between the fluids, causing pressure drop and characteristic flow patterns. This film flow was first described by Mersmann (45) in his attempt to derive general considerations on the hydrodynamic behaviour of random packings. Three different film flow profiles is identified at increasing gas flow rates, as can be seen in Figure 2- 3.

At low gas flow rates, seen in Figure 2- 3A, the shear force is too small to affect liquid flow significantly. A liquid velocity gradient of zero is observed at the phase boundary. Strong gas flow, as seen in Figure 2- 3B, causes significant interaction and a new velocity profile forms in the liquid. The liquid flow is somewhat hindered, but the net liquid flow is still in a downward direction. At very high gas velocities, as seen in Figure 2- 3C, the force exerted by the gas is sufficient to entrain the liquid. The liquid flow is significantly impeded and flooding occurs as soon as a net upward flow of liquid is reached. (46)

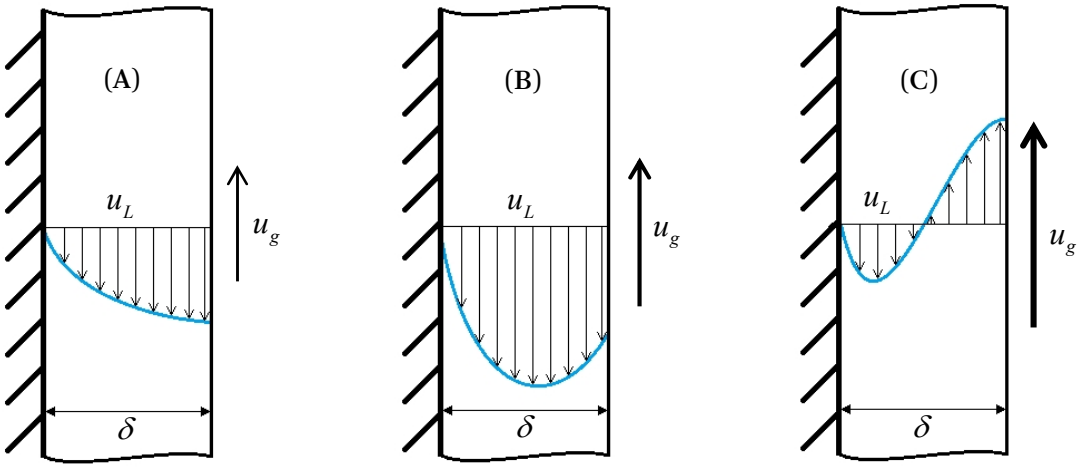


Figure 2- 3: Film flow with A) negligible, B) strong and C) very strong gas counterflow. Drawn from the worded definition by Tilton in Perry's Chemical Engineers' Handbook (46).

Between each of these film flow regions a point of change is defined as a reference. Firstly, the loading point, at which the force exerted by the gas on the liquid becomes significant and the rate of change in pressure drop starts to change. Secondly, the flooding point, where a finite change in the liquid or gas flow causes the column to flood or, theoretically, for pressure drop to tend to infinity (13; 47). There is not much to expand on for the loading point as it is clearly defined and easily measured. The flooding point, on the other hand, is a much more abstract concept and needs clarification.

2.2.4 Flooding

There is no universal definition for flooding and many of the definitions available in literature are vague, impractical or arbitrary (47). For example, it was stated in Section 2.2.3 that at the flooding point the pressure drop over a column tends to infinity (13; 47). This is a mathematically sound definition, but its application in practise is open to interpretation. Upwards of 20 different definitions of flooding exist (47), with each author presenting a definition in line with their own research. Typical definitions presents flooding as dependent of the liquid level above the packing (13), the amount of entrainment (48), the pressure drop over the column or other arbitrary visual observations.

Eckert (4) explains flooding with regard two different flooded states, namely classical flooding and operational flooding. Classical flood is defined as where the liquid phase is continuous, causing the pressure drop to tend to infinity. Operational flood defines the column in a non-steady state sometime before classical flooding occurs. This non–steady or unstable state is the crux of the flooding point, and even a single definition applied consistently can report different results for two experimental runs (49).

Regardless of the definition chosen, flooding is caused by two separate mechanisms (1):

- At small gas/liquid flow ratios where packings fill up with liquid, or,
- At high gas/liquid flow ratios where droplet entrainment becomes significant.

This translates into three different physical phenomena in the columns.

Firstly, flooding occurs when the bulk liquid flows upward, or entrainment and detainment in the column becomes large enough to prevent the majority of the liquid from flowing downwards. This causes a layer of liquid to form at the top of the packing, which continues to grow and may even be discharged from the gas lines at the top of the column.

Secondly, flooding can occur at the narrowest cross section in the column packing. This forms a 'bottleneck' which causes a local build-up of liquid. Eventually this liquid build-up will propagate up the column causing a state similar to that of the first flooding mechanism. This flooding type is especially likely in random packing, due to the intrinsically chaotic nature of the packing type.

Thirdly, flooding is described as the point where the shear force between the gas and liquid is larger than the gravitational force working in on the liquid, causing drops do be sheared from the liquid. These liquid droplets are carried up through the column and entrained out with the top product.

Flooding has a direct influence on the effectivity of a column. During mass transfer operation the effectivity of a column increases as it approaches the flooded state, as the throughput and interaction of the fluids is increased. When the column reaches a flooded state, its efficiency drastically decreases. Thus a column is ideally operated as close to the flooding point as practically possible without causing flooding. (1)

The propagation of a column from the flooding point to a fully flooded state is a gradual process and monitoring the pressure drop over a column can give advanced warning of flooding. Hence pressure drop is an important parameter in the control and operation of a column.

2.2.5 Pressure drop

The pressure drop over a column is one of the standard parameters measured in hydrodynamic investigations. It is measured over the column internals, with the highest pressure at the bottom of the column and the lowest at the top. It is dependent on the column internals, operating pressure, fluid properties and fluid flow rates and is easily measured and clearly defined. The pressure drop increases linearly with packed height for a specific type of packing and column diameter under the same operating conditions (1). With columns typically being of differing heights, the absolute pressure drop over a column is not a meaningful value and it is related to a unit length (e.g. Pa/m).

This pressure drop per unit length, $\Delta P/H$, has a direct relationship with the separation efficiency, n_t/H , of a column. This dependency was initially discovered by Kirschbaum (50) and is shown in Equations [3, 4].

$$\frac{n_t/H}{\psi_L} \cong 0.13 \qquad [3]$$

$$\frac{\Delta P}{H} = \psi_{VL} \times \frac{u_G^2}{2} \times \frac{\rho_G}{d} \qquad [4]$$

where n_t/H is the number of theoretical stages per 1 m of packed height, ψ_{VL} the total resistance coefficient, u_G is the gaseous phase velocity, ρ_G the gaseous phase density and d the column diameter.

Using these correlations, the pressure drop of a packing can be used to determine the column diameter needed for a specific application. Since Kirschbaum (50), correlating the pressure drop to efficiency has been further pursued by Billet and Mackoviak (51; 52; 53; 54).

As the pressure can be correlated with the separation efficiency, as shown in Equations [3, 4], it is used not only to predict flooding, but to determine the optimal operation point of the column. In the loading region, which will be discussed more thoroughly later in this section, efficiency increases with an increase in pressure drop. This trend typically continues up to the flooding point, whereafter the efficiency drops drastically. Heuristics state that a typical operating point of 70% (55; 56) of the flooding point is to be advised. This operating point can be determined by using a GPDC or Generalized Pressure Drop Correlation chart, the most common of these being the Sherwood-Lobo (44) correlation.

Dry and Wet Pressure Drop

The measurement of pressure drop is divided into a dry and a wet pressure drop (1). The dry pressure drop, $\Delta P_0/H$, is measured at a specific gas flow rate in the absence of liquids. This provides a benchmark of the pressure drop without two-fluid interactions, and hence without flooding and shear phenomena.

The wet or irrigated pressure drop, $\Delta P/H$, is measured during operation with both phases present. Here the fluids interact, exerting shear forces on each other, causing additional pressure drop over the column. The wet pressure drop is important when designing countercurrent systems, especially in determining the gas feed required (assuming the liquid rate is limiting). The gas feed rate governs the blower, compressor capacity for a stripping column and the reboiler pressure and column temperature in a distillation column, and hence a major part of the operating costs of a classical system. The wet pressure drop is generally used in correlations and equations describing hydrodynamics, as it represents actual operating conditions.

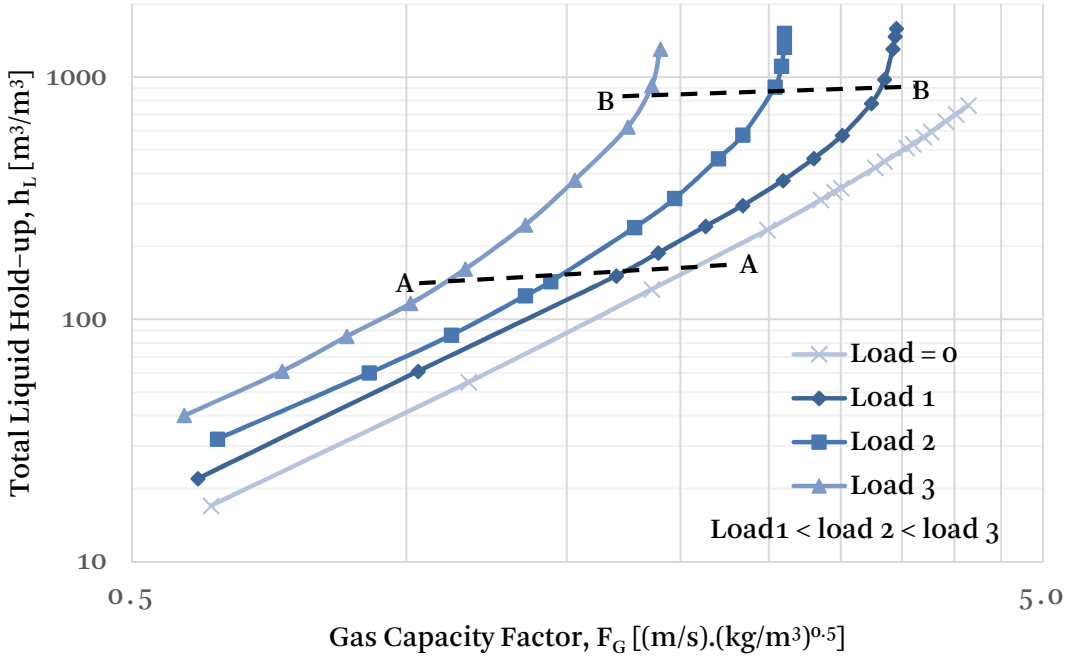


Figure 2- 4: Typical pressure drop vs. gas capacity factor.
Drawn from data by Lamprecht (2).

Typical wet and dry pressure drop curves can be seen in Figure 2- 4. The pressure drop is plotted against the gas capacity factor F_G, also called the vapour flow factor, which is defined as the gas velocity adjusted for the density of the gas. The gas capacity factor will be properly defined in Section 2.4.4, Equation [20].

- The pre-loading region: This region is defined as below the loading point of the system. The wet pressure drop in the system increases in a linear fashion, parallel to the dry pressure drop. The offset of the wet from the dry pressure drop is explained by the decrease in available cross-sectional area caused by the liquid flow, with higher liquid loads causing higher pressure drops at the same gas capacity factor. In Figure 2- 4 this flow regime is represented by the area below the A–A line, which represents the loading point.
- The loading region: Here the interaction between phases becomes significant, but not overpowering, and the resulting shear forces cause additional pressure drop. The rate of change in the pressure drop is no longer linear, but increases as a function of the gas capacity factor in this regime. This is represented as the area between the A–A and B–B lines, being between the loading and flooding points.
- The flooding region: The rapidly increasing pressure drop eventually yields a point where the value effectively tends to infinity. This is defined as the flooding point and any points beyond this are seen as being in the flooding region. The area beyond the B–B line falls within this flow regime.

Pressure Drop in Random and Structured Packings

At the same gas capacity factor the dry pressure drop behaves differently for random and structured packings. Apart from the obvious changes due to different geometries, each packing type responds differently to a change in column diameter. In a random packing the pressure drop is independent of the column diameter, while in structured packing the column diameter has been shown to have a significant effect (57; 58). The pressure drop over a column with structured packing drops with an increase in diameter. To this effect Maćkowiak (1) states that in structured packings: "The experimental pressure drop data for small columns can be up to 65% higher than for large columns". This statement is made with respect to normal industrial sized columns, not for high pressure and supercritical applications, and further research is needed to validate this for supercritical systems. As the columns used in supercritical extraction are usually small in diameter, as discussed in Section 2.2.2, this is an important phenomenon and merits further investigation when structured packings are considered.

2.2.6 Liquid Hold-up

If a column operating in the loading region exhibits an increase in the rate of change in pressure drop, it can be assumed that the shear forces between the phases have increased. If the shear forces increase while the liquid load to the column stays constant, the gas in the column will exert a net upward force on the liquid in the column. The system will then retain more liquid until the opposing force, exerted by gravity on the liquid, equals that of the upward shear force. Hence a new equilibrium is achieved by allowing the liquid inventory in the column to increase. (4)

This total retained liquid in a column is defined as the liquid hold-up. The liquid hold-up of a column, like the pressure drop, provides an indication of the hydrodynamic capacity of said column. Like the pressure drop it is also dependent on the column internals, operating pressure, fluid properties and fluid flow rates. It can then be further affected by the bottom liquid level in, and position of the gas inlet to, the column.

While the pressure drop gives an indication of the separation efficiency, the liquid hold-up is used to calculate mixture density, actual gas and liquid viscosities, effective viscosity, heat transfer and liquid residence time (1). As with the pressure drop, the liquid hold-up is normalized, in this case to the units of volume of hold-up per unit volume of packing, h_L (m^3/m^{-3}), to create a term that is translatable between systems.

Static and Dynamic Liquid Hold-up

The liquid hold-up is divided into a static and a dynamic hold-up, which can each be measured separately. The static hold-up is defined as the liquid that stays in the column, 'wetting' the column internals. This hold-up does not leave the column freely because of adhesion forces, or being trapped by packing geometry. The static liquid hold-up is a constant value for a specific experimental setup and fluid combination. The dynamic hold-up is the liquid in the column retained due to flow phenomena such as viscosity, surface tension and shear forces caused by phase interaction. The difference between the two types can be seen in Figure 2- 5.

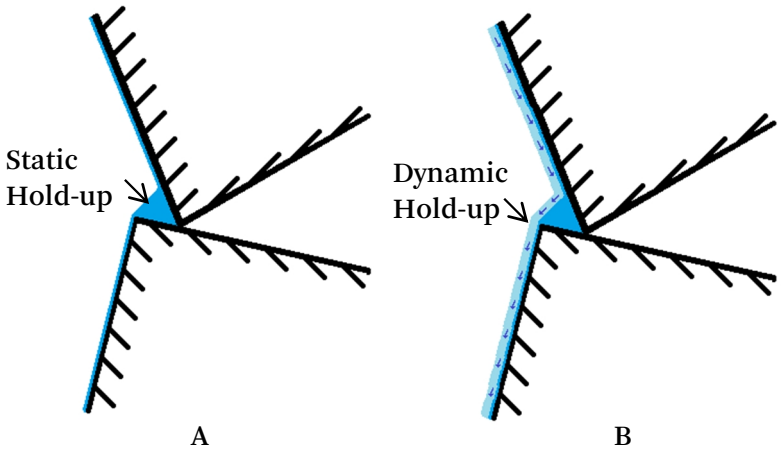


Figure 2- 5: A) Static hold-up only and B) Dynamic and static hold-up.

The static hold-up, h_{Ls}, as seen in Figure 2- 5A, is caused by the forces between the gas, liquid, the surface of the packing and, depending on the orientation, the effect of gravity. For static hold-up to occur these forces need to be in equilibrium. Said forces are in turn dependent on the liquid weight, surface tension, gravity and contact area. These factors can be lumped into a dimensionless number, the Bond number, Bo (59; 60). The original Bond number was intended for a moving sheet of water, flowing over a known length, and the equation is slightly modified for use in column geometry by substituting in the packing surface area per unit volume, a.

The Bond number is seen in Equation [5]:

$$Bo = \frac{g\rho_L}{\sigma a^2} \qquad [5]$$

where g is the gravitational constant, ρ_L the liquid density and σ the liquid surface tension. Correlations exist that relate the Bond number to the static liquid hold- up, h_{Ls}, (61) and will be discussed later in Section 2.4. It is unclear whether these correlations are applicable to high

pressure systems and further investigation is recommended. Typically the high density of the supercritical phase will have a bigger effect than in non-supercritical systems and an approach using the Bond number will have to be modified for the supercritical density.

The dynamic hold-up, h_{Ld}, constitutes the majority of the liquid in the column under normal operation. As can be seen in Figure 2-5B, the dynamic hold-up is in constant motion. Correlations used to describe the dynamic hold-up include the liquid Reynolds number and the Froude number, both modified for column flow.

Firstly, the Reynolds number is modified from the classical Reynolds number (62) to allow for use in a column. This is done by substituting the surface area per unit volume of packing in the place of the typical length. The modified formula is seen in Equation [4]:

$$\mathrm{Re}_L = \frac{\rho_L u_L}{\mu_L a} \qquad [6]$$

where u_L is the superficial liquid velocity and μ_L the dynamic liquid viscosity. The superficial liquid velocity is calculated by dividing the volumetric flow rate by the cross sectional area. This liquid Reynolds number, Re_L, provides a measure of the ratio of inertial and viscous forces in the liquid flowing over the column internals. If $\mathrm{Re}_L \geq 2$, the flow is expected to be turbulent with $\mathrm{Re}_L < 2$ indicating laminar flow (1). Note this is different to the classical gaseous Reynolds number where a pivot point of 2 000 is typical.

The liquid Froude number is as follows:

$$Fr_L = \frac{u_L^2 a}{g} \qquad [7]$$

The Froude number provides a measure of the ratio of inertial forces and gravity. Together the Reynolds and Froude numbers are used to predict the dynamic hold-up. This will be discussed in more detail in Section 2.4.2.

Adding the static and dynamic hold-up together yields the total liquid hold-up, h_L. To approximate the total liquid hold-up the Reynolds and Froude numbers can again be used. Equations predicting h_L are discussed in detail by Maćkowiak (1) and will not be discussed here.

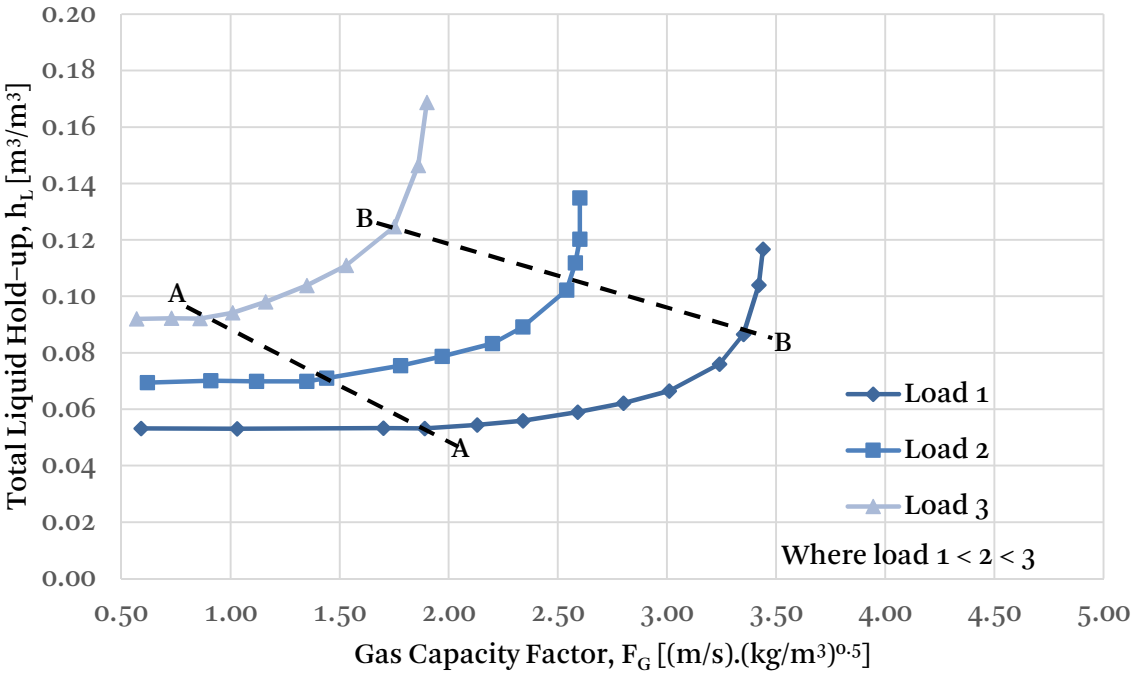


Figure 2- 6: Typical liquid hold-up vs. gas capacity factor.
Drawn from data by Lamprecht (2).

Typical liquid hold-up curves can be seen in Figure 2- 6. The liquid hold-up is plotted, like the pressure drop, against the gas capacity factor, F_G. As with the pressure drop, the trends in the liquid hold-up can also be correlated to the different film flow types, as described in Section 2.2.3. Keeping this in mind, the curves are divided into three flow regimes by the loading point, line A–A and the flooding point, line B–B. These flow regimes are described as follows (48; 47):

- The pre-loading region: The area below the loading point, A–A, where the interaction between phases are negligible. It can be seen in Figure 2- 1 that the liquid hold-up stays constant in this region, with offset between different liquid loads dependent on the liquid load itself.
- The loading region: Interaction between phases becomes significant, causing the gas flow to exert a significant force on the liquid. The liquid hold-up increases exponentially as a function of the gas capacity factor. This region is defined as between the loading point, A–A, and the flooding point, B–B
- The flooding region: Here the shear forces exerted by the gas become overpowering and the liquid is entrained upwards in the column. The liquid hold-up rises sharply and effectively tends towards infinity. This is defined as the flooding region and encompasses any points beyond the flooding point, B–B.

Droplet Entrainment

High gas flow rates cause high shear forces between the liquid and gas phases. When these shear forces exceed the downward forces a net upward flow of liquid occurs, as discussed for film flow in Section 2.2.3. In some cases the shear force exceeds the cohesive forces of surface tension and viscosity in the liquid, causing loose droplets to be sheared from the falling liquid film. These droplets are then carried along with the gas flow until they rejoin a falling film, collide with a column internal or get carried out of the column with the exiting gas. The latter of these three possibilities can lead to the presence of unwanted components in the top gas product. As the purpose of a column is to effect a separation of some sort, this phenomenon is highly undesirable, leading to a decrease in efficiency. The packing geometry has a direct impact on entrainment, with smaller elements decreasing the degree of entrainment. (1)

2.3 Supercritical Two-Phase Countercurrent Hydrodynamics

2.3.1 Introduction

Hydrodynamics under supercritical conditions can be roughly divided into the hydrodynamics around falling films, being the more fundamental approach, and column hydrodynamics, being the consideration of the overall hydrodynamic effect during column operation. Of the two, column hydrodynamics is more directly relevant to industrial use and practical application and will be discussed here. As there is relatively little data available in literature, each of the contributions found will be discussed individually, followed by a summary of the findings in Table 2- 1. For the sake of ease of reading the column sizes and packing types are not mentioned in the survey, but only summarised in Table 2- 1. Next the trends expected in supercritical hydrodynamic data will be summarised, followed by a brief discussion of numeric/algebraic hydrodynamic approximations and the effect of mass transfer on hydrodynamics.

2.3.2 History of Hydrodynamics under Supercritical Conditions

The earliest paper found dealing with supercritical extraction in packed columns is that of Peter and Tiegs (63), as referenced by Rathkamp, et al. (64). This paper was presented at a conference in 1984, and although no mention of hydrodynamics is made, the study showed that supercritical fluid extraction can achieve high degrees of efficiency in packed columns.

The first paper found considering high pressure hydrodynamics in packed columns was by Krehenwinkel and Knapp (65), published in 1987. This paper measured pressure drop and flooding in an assortment of random packings. Although this research used nitrogen (and not

in the supercritical phase) it is worth mentioning as it is a very thorough hydrodynamic study concerned with a high pressure, high density gaseous phase.

Rathkamp, et al. (64) in 1987, followed closely by Seibert and Moosberg (10) in 1988, conducted research into the efficiency and energy requirements of columns operating with supercritical CO_2. Rathkamp, et al. tested a dispersed gas phase column packed with Raschig rings and a spray column setup, finding the spray column to be the more efficient of the two. Seibert and Moosberg tested a column with sieve trays, Raschig rings, intalox saddles and a spray column setup, finding the sieve trays to be the most efficient and the spray column the least efficient. With respect to hydrodynamics, Seibert and Moosberg measured the dynamic liquid hold-up for a CO_2-isopropanol-water system. These two publications, while not yielding much value in the field of hydrodynamics, are of interest as they consider an overall view of the technology and show the trials and errors of early research. A multitude of publications exist on the treatise of mass transfer and efficiency, but will not be discussed here for the sake of relevance and brevity.

The first hydrodynamic research on a structured packing, specifically Montz-pak type A3, was done by Sievers (66) in 1994, followed by Woerlee (67) in 1997, working on the same experimental setup. It was found by these authors that the measured flooding data points were not consistent with generalized pressure drop correlations, such as those proposed by Sherwood-Lobo (44) and Souders and Brown (68). This was attributed to the high solubility of CO_2 in the liquids used, namely water and hexadecane. This illustrated the need of systems with low mutual solubility to determine the basic fundamental hydrodynamics, as will be discussed more thoroughly in Section 2.3.5.

Lim, et al. (69) in 1995 investigated the mass transfer and liquid hold-up for an unnamed, knit mesh structured packing with an ethanol/water/CO_2 system. It was found that higher liquid hold-ups were observed at higher pressures.

As earlier research had problems isolating hydrodynamics, due to high mutual phase solubility, research shifted to systems with less soluble organic oils. Although this was not the explicit intention of the research done by Machado (70) in 1998, it was a step in the right direction. Machado studied flooding using a palm oil distillate/CO_2 system with Sulzer EX laboratory packing and successfully measured flooding points consistent with the work by Woerlee (67). On the same column Budich (71; 72) investigated flooding in orange peel oil/CO_2 and water/ethanol/CO_2 systems. It was found that the orange peel oil exhibited similar trends as earlier research (67; 70), but the water-ethanol systems flooded much earlier than expected. The earlier flooding was attributed to the large density differences between water (1 g/ml),

orange oil (~0.84 g/ml) and ethanol (0.79 g/ml), with the fluids with densities closer to the supercritical fluid density flooding later.

The first truly thorough investigation into hydrodynamics under supercritical conditions was by Meyer (73) in 1998, using soybean oil/CO_2 and fish oil/CO_2 systems, using the same experimental setup as Machado (70) and Budich (72). Meyer not only measured the flooding point, as done by previous authors, but also the pressure drop and physical properties of the systems. Further Meyer (73) compared his results with well-known flood point correlations of the time, namely those by Mersmann (45), Eckert (74) and Maćkowiak (75), stating explicitly for the first time that the models applicable at vacuum and normal pressures do not readily predict high pressure systems (P > 70 bar).

The next contribution to the field was also a significant one, being the Ph.D. dissertation of Stockfleth (76). The core research of his work was summarised in two papers, published in collaboration with Brunner, in 1999 and 2001 (14; 13). They investigated liquid hold-up, flooding, pressure drop and foaming for water/CO_2, olive oil distillate/CO_2 and tocopherol/CO_2 systems. Stockfleth and Brunner (13) concluded that supercritical fluid hydrodynamics are not fundamentally different from those at atmospheric pressure. The data collected were fitted with relative success to dry pressure drop, liquid hold-up and flooding data correlations adapted for the supercritical density. The correlations used will be discussed in more detail in Section 2.4. Furthermore Stockfleth, et al. (14) confirmed the earlier assumption of Budich (71; 72) that flooding is primarily dependent on the density of the liquid phase and packing geometry. Finally it was found that foamability decreased decisively with increasing pressure, making it effectively negligible under certain conditions. Although it was not concluded by Stockfleth, et al. (13), it can be deduced that this decrease in foamability is due to the decrease of liquid surface tension at high pressures.

After the work of Stockfleth and Brunner only one further investigation into supercritical fluid hydrodynamics has been done by Zacchi, et al. (77), which investigated efficiency and static and dynamic hold-up for a rapeseed oil/CO_2 system. The findings of this paper are in agreement with those of Stockfleth, et al. (14; 13).

A summary of the above discussion can be seen in Table 2- 1 on the following page. To provide a better view of the literature reviewed the column diameter, packing used, packed height, binary system, pressure and temperature tested is listed.

2.3.3 Trends Expected

Summarising from the publications discussed in Section 2.3.2, the following trends are expected in supercritical fluid hydrodynamics:

- Dry pressure drop will:
  - Increase with higher supercritical solvent feed rate.
  - Be higher than that of the same system at atmospheric conditions due to the elevated density/viscosity of the supercritical phase.
- Wet pressure drop will:
  - Increase with higher supercritical solvent or liquid feed rate.
  - Be higher than the respective atmospheric dynamics due to the elevated density/viscosity of the supercritical phase.
- Liquid hold-up will:
  - Increase with higher supercritical solvent or liquid feed rate.
  - Be primarily dependent on the liquid density.
  - Static hold-up typically decreases at high pressure due to the reduction in liquid surface tension (13).
  - High supercritical phase density produces significant buoyancy (13), which leads to higher total liquid hold-up than the respective atmospheric values.
- Flooding:
  - Mutually dependent on the liquid and supercritical phase flow rates. For example, if liquid load 1 < load 2, then the system with load 2 will flood at a lower supercritical phase flow rate than that of the system with load 1. The inverse is also true, with the hypothetical supercritical load 1 < load 2, then load 2 will flood at a lower liquid flow rate than load 1.
  - Is primarily dependent on liquid density, according to Stockfleth, et al. (14). Thus systems with higher liquid densities will flood sooner.
- Foaming:
  - Is assumed negligible in supercritical extraction columns (13), as foamability decreases decisively with increasing pressure.

Table 2- 1: Historically relevant investigations showing column diameter, packing type and height, liquid and supercritical phases and temperature and pressure ranges.

Author(s) and Year Published	Column Inner Diameter	Packing Used	Packed Height	Liquid Phase	Supercritical / Gas Phase	Pressure (Bar)	Temperature (K)
Systems investigating Hydrodynamics							
Krehenwinkel and Knapp (64) - [1987]	86mm - 155mm	15 mm Raschig rings 15 mm Pall Rings 10 & 15 mm Berl Saddles 20 mm Novalox Saddles	0.8 - 1.8 m	Metanol Water Glycol	Nitrogen	1.2 - 100 Bar	190 - 300 K
Seibert and Moosberg (10) - [1988]	98.8 mm	12.7 mm Raschig rings no. 15 Intalox saddles	1.68m	Isopropanol - Water	Carbon Dioxide	82 - 152 Bar	297 - 318 K
Sievers (65) - [1994]	36 mm	Montz-pak type A3	2 m	Water	Carbon Dioxide	114 - 220 Bar	323 K
Woerlee (66) - [1997]	36 mm	Montz-pak type A3	2 m	Hexadecane	Carbon Dioxide	80 - 173 Bar	323 - 343 K
Lim, et al. (68) - [1995]	31.8 mm	Knit mesh packing	1.5 m	Ethanol - Water	Carbon Dioxide	91 - 122 Bar	308 - 323 K
Machado (69) - [1998]	25 mm	Sulzer EX	1 m	Palm oil distillate	Carbon Dioxide	200 - 290 Bar	333 - 373 K
Meyer (72) - [1998]	25 mm 35 mm	Sulzer EX Sulzer CY	1 m	Soybean oil Fish oil	Carbon Dioxide	100 - 300 Bar	313 - 393 K
Budich and Brunner (70, 71) - [1999]	25 mm	Sulzer EX	1 m	Orange peel oil	Carbon Dioxide	100 - 112 Bar	323 - 343 K
Stockfleth and Brunner (76) - [1999] ; (45, 75) - [2001]	25 & 35 mm	5 x 0.5 mm Raschig rings 15 mm Berl Saddles Sulzer CY Sulzer EX	0.9 m	Water α-Tocopherol Olive oil deodorizer distillate	Carbon Dioxide	80 - 300 Bar	313 - 373 K
Zacchi, et al. (77) - [2008]	40 mm	Sulzer Mellapak 500.X 6 mm Wire mesh random packing manufactured	7.5 m	Rapeseed oil doped with Oleic acid	Carbon Dioxide	200 - 260 Bar	333 K
Systems investigating efficiency and other noteworthy systems							
Peter and Tiegs (62) - [1984]	25.4 mm	Raschig rings Drop distributor Split-tube Wire spirals Sulzer gauze packing	-	Oleic acid glycerides with Acetone entrainer	Carbon Dioxide	137 Bar	343 K
Rathkamp, Bravo and Fair (63) - [1987]	25.4 mm	6.4 mm Raschig rings	0.61 m	Ethanol - Water Isopropanol - Water	Carbon Dioxide	103 Bar	308 - 313 K

2.3.4 Numeric and Algebraic Approximations

As supercritical pilot plants are not widely available and cheap to construct, sources of new data are limited. This, along with increased use of computers and computational techniques, has led to the modelling of supercritical systems becoming more common. Although most of the modelling done is on mass transfer and thermodynamics (78; 79; 80; 81), simulations investigating hydrodynamics can be found.

Most relevant to this project is the work done by Fernandes, et al. (82; 83), investigating the wet and dry pressure drop over a Sulzer EX packing using a commercial CFD (Computational Fluid Dynamics) software package, *Fluent*. Results obtained were compared with the experimental results of Meyer (73) and Stockfleth and Brunner (14; 13) and found to correlate very well. No simulations concerned with random packing were found.

2.3.5 The Effect of Mass-Transfer

It is important to remember that the ultimate goal of a packed column is to effect mass transfer. In the case of supercritical fluid extraction in columns the goal is typically to strip a component from a liquid or to purify a product, making the process analogous to a standard stripping or rectification column. It can also be argued that the high density of the supercritical phase yields a process that is closer to liquid-liquid extraction. Indeed supercritical extraction has elements of both these extraction types due to the inherently dual nature of the supercritical fluid itself.

Numerous investigations into supercritical mass transfer exist with widespread research into phase equilibria (84; 85; 86; 87) and mass transfer phenomena. No single conclusive correlation for supercritical mass transfer has been developed (5). Although mass transfer is the final goal, hydrodynamics stay relevant as a fundamental of column design.

As briefly mentioned in Section 2.3.2, mass transfer is to be either limited or fully accounted for during hydrodynamic investigations. This is because mass transfer directly affects both phases' flow rate and properties of both phases, such as viscosity and surface tension, which in turn has a direct influence on column hydrodynamics. Mass transfer depends on the components present in the system and the degree of solubility. Supercritical fluid systems typically possess mutual solubility, meaning that both phases will contain some of the other phase in solution. This mutual solubility affects the properties of both phases, causing a larger range of possible deviations, and ultimately complicating the interpretation of hydrodynamic results. This is where the selection of an appropriate liquid/supercritical fluid system becomes important to eliminate the solubility affecting at least one on the phases.

2.4 Semi-Empirical Correlations for Hydrodynamics under Supercritical conditions

As stated in Section 1.1, modified subcritical correlations have been used with relative success to approximate supercritical column design, even though they do not allow for the higher density, viscosity and surface tension of a supercritical fluid. These correlations provide an approximate prediction of the hydrodynamics, which, along with a predominant culture of overdesign in engineering, provides a workable solution for industry. This culture of overdesign leads to high initial costs, especially in the high pressure environment required for supercritical fluids, making the solution less attractive (see Section 2.1.3). A step in the right direction was the work of Stockfleth and Brunner (13; 14) (discussed in Section 2.3.2). They suggested equations modified for the density of the supercritical phase, providing a better approximation of hydrodynamics under supercritical conditions.

For the approximation of hydrodynamics in packings, three different model structure simplifications are typically considered, being the channel, beam and particle models (88; 13). The channel model visualizes the packing as a solid body with a number of equally spaced, round channels running through the packing from top to bottom. This model fails for high surface area packings, where the calculated channels start to overlap in order to emulate the large surface area. The beam model is the exact opposite of the channel model, being a void space filled with equally spaced solid round beams. This model, being of similar nature as the channel model, falls victim to the same shortcomings. The particle model sees the packing as a bed of round spheres with the sphere or particle diameter, d_p, calculated as in Equation [6]:

$$d_p = 6\frac{1-\in}{a} \qquad [8]$$

where $\in$ is the fractional void volume and a the packing surface area per unit volume as first defined in Equation [5].

The following discussions on semi-empirical models are based on the particle model to correspond with the work of Stockfleth, et al. (13; 14), using the models originally proposed by Stichlmair, et al. (89). Other correlations than the ones discussed here are available in abundance (1) for standard hydrodynamics, but they are not applicable for the small diameters typically used in supercritical columns and in this study and no modifications to be applicable at supercritical conditions have been made.

2.4.1 Dry Pressure Drop

The dry pressure drop, as first discussed in Section 2.2.5, can be calculated with a modified Ergun-type equation (88). The Ergun equation expresses the friction factor in a packed column as a function of the Reynolds number. To calculate the friction factor itself, a modified version of the original equation proposed by Stichlmair, et al. (89), is used. This modification states that the friction factor, ψ, is proportional to $\in^{4.65}/(1-\in)$ instead of $\in^{3}/(1-\in)$. Assuming that this is correct, the friction factor, and from there the pressure drop, is calculated using Equation [9]:

$$\psi = \frac{K_1}{\mathrm{Re}_G} + K_2 = \frac{4}{3}\frac{\Delta P_0 \in^{4.65} d_p}{H(1-\in)\rho_G u_G^2} \quad \text{or} \quad \frac{\Delta P_0}{H} = \frac{3\psi\rho_G u_G^2(1-\in)}{4 d_p \in^{4.65}} \qquad [9]$$

where $\Delta P_0/H$ still defines the pressure drop per unit length of dry packing and ρ_G and u_G is the respective density and superficial velocity of the supercritical phase. The superficial velocity is calculated by dividing the volumetric flow rate by the column cross sectional area. K_1 and K_2 are empirically determined constants that are dependent on the geometry of the packing used.

The gaseous phase Reynolds number, Re_G, as used in Equation [10], is defined as:

$$\mathrm{Re}_G = \frac{u_G d_p \rho_G}{\mu_G} \qquad [10]$$

where μ_G is the dynamic viscosity of the gaseous phase.

Constants K_1 and K_2 are determined by fitting experimental data to Equation [9]. This provides a generalized empirical equation capable of predicting the dry pressure drop for a specific packing. In consulting literature the only constants found for random packing is for 5 mm Berl saddles and 5 x 0.5 mm Raschig rings by Stockfleth, et al. (13). The values determined in their study for the empirical constants are $K_1 = 23$ and $K_2 = 1.2$ and provides a reasonable, although far from perfect, fit on the data gathered by Stockfleth.

2.4.2 Liquid Hold-up below the Loading Point

Liquid hold-up below the loading point is dependent on the interaction between the liquid and the packing, as explained in Section 2.2.6. Also discussed in Section 2.2.6 is the fact that liquid hold-up consists of a static and a dynamic element.

First the static hold-up is discussed. The static hold-up is a function of the dimensionless Bond number, as discussed in Section 2.2.6, Equation [5],

$$Bo = \frac{g\rho_L}{\sigma a^2} \qquad [5]$$

and is dependent on gravity, g, liquid surface tension, σ, liquid density, ρ_L, and the packing surface area, a. The static hold-up is approximated as follows:

$$h_{Ls} = 0.037 \in Bo^{-0.07} \text{ for } Bo < 1 \qquad [11]$$

$$h_{Ls} = 0.037 \in Bo^{-0.65} \text{ for } Bo \geq 1 \qquad [12]$$

The surface tension of a liquid is generally very low at high pressures (13), implying that the Bond number would have a high value. This in turn means a small static liquid hold-up, leading to the static hold-up being considered negligible during further modelling. It is, however, important to adjust the particle diameter and specific surface area if the packing is liable to form dead volumes, like Raschig rings. This problem has been eliminated in modern random packings, but if more information is required the book by Maćkowiak, *Fluid Dynamics of Packed Columns*, (1) is suggested.

The dynamic liquid hold-up below the loading point is predicted using the Reynolds and Froude numbers of the liquid phase (see Section 2.2.6, Equations [6, 7]). The dynamic hold-up below the loading line is simply calculated as follows:

$$h_{Ld,0} = K_3 \left(\frac{Fr_L^2}{\mathrm{Re}_L} \right)^{K_4} \qquad [13]$$

where K_3 and K_4 are empirical parameters that are determined with an experimental data fit. Again no empirical parameters were found for small diameter random packings for this correlation, except the parameters determined by Stockfleth, et al. (13) for Raschig rings and Berl saddles, $K_3 = 1.27$ and $K_4 = 0.23$. In contrast K_3 is reported as $K_3 = 1.6$ in the doctoral thesis of Stockfleth (76), again providing a reasonable, but not perfect fit to the data gathered.

2.4.3 Wet Pressure Drop and Liquid Hold-up above the Loading Point

Above the loading point the liquid hold-up and pressure drop become interdependent. This is due to the interaction between the liquid and gaseous phases becoming significant, as discussed in Sections 2.2.5 and 2.2.6. Still following the work of Stichlmair, et al. (89), the irrigated or wet pressure drop per unit length, $\Delta P / H$, is calculated as:

$$\Delta P / H = \Delta P_0 / H \{[1- \in (1 - h_{Ld} / \in)] / (1- \in)\}^{(2-K_1/\psi)/3} . (1 - h_{Ld} / \in)^{-4.65} \qquad [14]$$

where K_1 and ψ is the same as that defined in Equation [9]. Note in the article by Stockfleth, et al. (13) this formula is reported incorrectly, even though it was applied correctly.

The dynamic liquid hold-up, h_{Ld}, is calculated in Equation [15]:

$$h_{Ld} = h_{Ld,0} \left[1 + K_5 (\Delta P / H . \rho_L . g)^{K_6} \right] \qquad [15]$$

with K_5 and K_6 yet a further set of empirically determined constants. The equation proposed by Stockfleth, et al. (13) differs from the original equation by Stichlmair, et al. (89) by substituting the liquid density, ρ_L, for the density difference between the liquid and supercritical phases, $\Delta\rho$, as can be seen in Equation [16]:

$$h_{Ld} = h_{Ld,0} \left[1 + K_5 (\Delta P / H . \Delta\rho . g)^{K_6} \right] \qquad [16]$$

This substitution is to compensate for the significant buoyancy force exerted by the supercritical fluid on the liquid phase. This buoyancy force works upwards against the force of gravity, substantiating the difference between the phase densities as an appropriate substitution.

To calculate the pressure drop Equation [16] is substituted into Equation [14], yielding an equation dependent only on pressure drop as variable. This equation can be solved iteratively to provide a pressure drop value and can be seen in Equation [17]:

$$\frac{\Delta P}{H} = \frac{\Delta P_0}{H} \frac{\left(\left[1 - \varepsilon \left(1 - {h_{L0}}/{\varepsilon} \left\{ 1 + K_5 \left({\Delta P}/{H \Delta\rho g} \right)^{K_6} \right\} \right) \right] (1 - \varepsilon)^{-1} \right)^{\frac{2-K_1/\psi}{3}}}{\left(1 - {h_{L0}}/{\varepsilon} \left\{ 1 + K_5 \left({\Delta P}/{H \Delta\rho g} \right)^{K_6} \right\} \right)^{4,65}} \qquad [17]$$

Once again no empirical parameters were found for small diameter random packings except the parameters determined by Stockfleth, et al. (13) for liquid hold- up. The data presented by Stockfleth, et al. (13) is very scattered and presented difficulty in presenting a clear, accurate model fit, leading to two fits presented to predict the flooding and liquid hold-up separately. Empirical constants determined for Raschig rings and Berl saddles are $K_6 = 2.0$, with $K_5 = 4.1$ for normal hold-up data and $K_5 = 8$ for flooding regime hold-up data. It should be noted that K_6 was not calculated by Stockfleth, et al., but rather chosen as an educated guess and kept constant to simplify the problem. No prediction of pressure drop values was attempted by Stockfleth.

2.4.4 Flooding

Flooding, as discussed in Section 2.2.4, is defined by Stockfleth, et al. (13) as the point where a finite change in gas or liquid velocity causes an infinite change in the pressure drop or liquid hold-up. Mathematically this translates to where:

$$\frac{\delta \Delta P}{\delta \Delta P_0} = \infty \Leftrightarrow \frac{\delta \Delta P_0}{\delta \Delta P} = 0 \qquad [18]$$

To attempt a prediction of the flooding point Stockfleth, et al. (13) determined the derivative of Equation [17] and equated it to zero in Equation [19]:

$$0 = \left(\frac{\Delta P}{H \Delta \rho g}\right)^{-K6} - \frac{2.65 K_5 K_6 h_{Ld,0}}{\in -h_{Ld,0}\left[1 + K_5\left(\frac{\Delta P}{H \Delta \rho g}\right)^{K_6}\right]} - \frac{\left(\frac{2 - K_1/\psi}{3}\right) K_5 K_6 h_{Ld,0}}{1 - \in + h_{Ld,0}\left[1 + K_5\left(\frac{\Delta P}{H \Delta \rho g}\right)^{K_6}\right]} \qquad [19]$$

Unfortunately this model, although it is mechanistic in nature with a solid physical background, provided a very poor prediction of the flooding point data gathered by Stockfleth, et al. (13).

No other successful correlation predicting flooding at supercritical conditions was found in literature. As an alternative Stockfleth, et al. (13) had relative success with a modified empirical Sherwood flooding diagram (3) used in conjunction with a correlation for flooding in pipes derived by Wallis (90). The correlation by Wallis, as restructured by Woerlee (67), can be seen in Equation [20].

$$F_G = \sqrt{H.g}\,\frac{K_7^2}{(1+K_4\sqrt{\Phi})^2} \qquad [20]$$

with F_G being the gas capacity factor and Φ the flow parameter.

The gas capacity factor, F_G, as mentioned in Section 2.2.5, defined as:

$$F_G = u_G(\rho_G / (\rho_L - \rho_G))^{0.5} \qquad [21]$$

and the flow parameter, Φ, is defined as:

$$\Phi = L / G(\rho_G / \rho_L)^{0.5} \qquad [22]$$

where L is the liquid phase superficial mass flow rate and G the gaseous phase superficial mass flow rate. Both of these terms are calculated by dividing the phase mass flow rate by the cross sectional area of the column.

2.5 Literature Shortcomings in Hydrodynamics under Supercritical Conditions

In the evaluation of the available literature and semi-empirical approximations, several important shortcomings can be identified. Focusing first on the existing literature, the following points of interest emerge.

Looking at the history of hydrodynamics under supercritical conditions, Section 2.3.2, it was seen that very little experimental work has been done on the hydrodynamics of supercritical systems. From the systems that were investigated a few areas of understanding can be identified that lack the necessary depth. Firstly, most of the studies fail to consider the effect of the mutual phase solubility in supercritical systems. If the solubility effect is mentioned it, is often not incorporated into work, and solubilities as high as 40 wt% (gaseous phase into liquid) deemed to have no effect on the properties of the system. This is a risky assumption, as the properties of fluids with supercritical fluids have been shown to vary significantly with pressure, which would in turn magnify the effect of any solutes in the supercritical fluid. No system fully negating the effect of mass transfer was found in literature.

Secondly, precious little work has been performed on random packings in supercritical conditions and none on modern random packings. For the small diameter columns typically used in supercritical columns random packing provides a significantly cheaper solution when compared to very expensive structured packings. Furthermore, structured and random

packings are known to react differently to column diameter, as discussed in Section 2.2.5, with random packings influenced less negatively by column diameter.

Thirdly, no investigation has been made into the effect of column diameter on hydrodynamics under supercritical conditions. At small diameters wall effects should be significant. No hydrodynamic studies have been performed on columns below 25 mm $Ø_l$.

Finally, hydrodynamic studies have only been performed with CO_2 as the working fluid. This limits the applicability of available hydrodynamics.

Looking at the semi-empirical approaches to hydrodynamics under supercritical conditions, as discussed in Section 2.4, some further issues are identified. Firstly, very limited empirical constants are available for the equations used, with only Raschig rings and Berl saddles fitted for random packings. Secondly, no universal models exist that predict supercritical flooding, even though hydrodynamics under supercritical conditions have been said to be fundamentally no different than atmospheric hydrodynamics (13). Thirdly, no allowance is made in the correlations for the higher viscosity and surface tension of the supercritical fluid and it is not even mentioned if these properties are considered significant or not. Finally, and most importantly, is that the semi-empirical correlations have only been proven on a few select systems, and only for a limited range of fluid properties.

Simply put, these shortcomings force industry to perform expensive and lengthy pilot plant studies in order to obtain a reliable design. In order to fill these gaps in literature, further hydrodynamic data are required. To do this a pilot plant setup, able to measure hydrodynamics under supercritical conditions systematically, is required.

2.6 Pilot Plant Investigation

As the shortcomings in the existing literature have been identified in Section 2.5, the next step is to perform experiments and gather data to fill said knowledge gap. Although supercritical pilot plants are available at the research facility, they are not geared for the measurement of hydrodynamic data. To measure hydrodynamics a pilot plant should be able to measure the pressure drop over a packed bed, provide a wide range of controlled liquid and supercritical fluid flow rates and measure the liquid hold-up, all under stable supercritical conditions. The existing plants have to be modified to conform to these requirements or a new plant has to be purchased or constructed.

To make an informed decision, and to acquire supercritical pilot plant design knowledge, research was done into pilot plants described in literature or available commercially.

2.6.1 University of Stellenbosch – Resident Pilot Plants

Two existing pilot plants with packed columns are present at the University of Stellenbosch. The first pilot plant consists of a 5 m high, 28 mm internal diameter ($Ø_I$) column, a separator and a solvent recovery system with a maximum column pressure of 260 bar. At the time of this study this pilot plant was used for other projects and not available as an option for this study. As a point of interest the pilot plant P&ID and description can be seen in Appendix A, A.1.1.

The second pilot plant was originally manufactured in 1990 by the company SITECH-Sieber and extensively modified first by the original owner SASOL, and later by the University. It consists of a 2 m high, 38 mm $Ø_I$ column and a 4.3 m high, 18 mm $Ø_I$ column, an 11 ℓ separator and a solvent recovery system. The pilot plant was originally designed to be shipped in a container and is very compact. Subsequent modifications have been done haphazardly and the plant has become cramped, leading to difficulties in accessing key components. This makes the plant less ideal for retrofitting. In addition to supercritical CO_2 this pilot plant can handle Ethane, Propane and LPG as a solvent. A flow diagram and short worded description of the pilot plant can be found in Appendix A, A.1.2.

2.6.2 The University of Texas at Austin

The University of Texas at Austin pilot plant setup is an example of an early research pilot plant. This pilot plant, used in the late 1980s, was very advanced for its time and possesses features that would be an asset for any research pilot plant, even today. An array of flow meters and buffer tanks serves to create a stable, well-functioning plant. The system had two identical columns of 98.8 mm $Ø_I$ and a packed height of 1.68 m, with one column fitted with sight glasses, yielding a maximum pressure rating of 103 bar and one without sight glasses with a maximum rating of 208 bar. Two online gas chromatography units were used to analyse the stream compositions during experimentation. A P&ID diagram and description of the process can be found in Appendix A, A.2.

2.6.3 Technical University of Hamburg, Harburg

The Technical University of Hamburg, Harburg has delivered a wealth of hydrodynamic and supercritical studies and has a longstanding reputation for fine supercritical work (13; 70; 71; 72; 73; 14; 76). The pilot plant used by them has been constructed in-house and consists of a 1.89 m high column with a variable diameter of 25 to 50 mm. A maximum pressure and temperature of 365 bar and 120°C is reported (76). A P&ID diagram and description of the process can be found in Appendix A, A.3.

2.6.4 SITEC-Sieber Engineering AG

The SITECH-Sieber company is a common name in high pressure supercritical solutions. The company recommended a standard pilot plant for the rough price of CHF 270,000 or ZAR 3 240 000 (calculated at the rounded exchange rate of 1:12 at time of writing) as given during correspondence. This plant consists of a 2 m high, 38 mm $Ø_I$ column, 1 ℓ solid extraction vessel, a separator and solvent recovery system. A maximum operating pressure and temperature of 300 bar and 200°C is reported. This setup cannot yet measure hydrodynamic data, but the required equipment can be specified for additional costs. The relevant documentation and P&ID for the suggested pilot plant can be viewed in Appendix A, A.4.

2.6.5 SepareCo

SepareCo is an Italian supercritical equipment company that claims automation and custom controllers as a selling point. A standard multipurpose supercritical pilot plant from this company includes a 4 m high, 32 mm $Ø_I$ column, 3 ℓ solid extraction vessel, a pasteurisation reactor, a separator and solvent recovery system, among others. A maximum operating pressure and temperature of 550 bar and 85°C is reported. A rough price estimate of EUR 360 000 or ZAR 5 220 000 (calculated at the rounded exchange rate of 1:14.5 at time of writing) was given during correspondence. A brochure for this pilot plant can be viewed in Appendix A, A.5.

2.6.6 Separex

Separex is based in France and provides compact, modern multipurpose pilot plants. The supercritical column setup from this company can fit into an area of only 1.5 x 0.8 x 2.5 m, providing a very compact solution. This includes a 2 m, 38 mm $Ø_I$ column with sight glasses, cyclonic separators and solvent recovery system. A rough price estimate of EUR 96 000 or ZAR 1 392 000 (calculated at the rounded exchange rate of 1:14.5 at time of writing) can be seen in the documents provided by Separex in Appendix A, A.6. This price includes operator training at the client site and a two year guarantee.

2.6.7 Flavex Aromats India Ltd.

The Flavex Aromats India division designs and builds tailor made pilot plants. Despite their primary focus in solid extraction systems the company quoted for a columned liquid extraction system. The supercritical system quoted by them includes a 4 m, 40 mm $Ø_I$ column, 1 ℓ separator, and a solid recovery system. A rough price estimate of USD 115 000 or ZAR 1 265 000 (calculated at the rounded exchange rate of 1:11 at time of writing) can be seen in the offer provided by Flavex in Appendix A, A.7.

2.6.8 Retrofitting vs. New Pilot Plant

Retrofitting one of the existing plants should prove the cheapest option, as no major purchases are needed and the labour can be performed at the departmental workshop. As noted in Section 2.6.1, the first pilot plant is not available for this study, while the second pilot plant is not suitable for retrofitting.

A new pilot plant is an expensive option, with the cheapest still costing well over a million South African Rand. The pilot plant will then still have to be adapted for hydrodynamic studies. As the significant funds required for such a purchase is to be avoided this is not seen as a viable option.

This leads to the alternative option of building a new pilot plant in-house. This is cheaper than buying a new pilot plant, as all of the design work and the majority of the labour can be performed at the departmental workshop.

2.6.9 Conclusion of the Investigation into Pilot Plants

Commercially available pilot plants are not rigged to measure hydrodynamics and would require expensive additional specification or aftermarket modification. Additionally, a new plant is exceedingly expensive and not a viable option for this study. The one pilot plant currently available at the research facility is outdated, cramped and cannot fulfil the needs of this study. Building a new pilot plant would be cheaper than buying a pilot plant, but still more expensive than the budget allows for.

In order to find an optimum solution it was decided to dismantle the existing one pilot plant and construct a new pilot plant in-house, using the major pieces of equipment from the old pilot plant. This would keep costs down and provide a new pilot plant customized for the needs of this and future studies.

In addition to keeping costs down, this option allows the construction of an effectively new pilot plant. This means that the pilot plant can be designed to not only meet the needs of this study, but also the needs of possible future research, which includes supercritical extraction, fractionation and solid extraction possibilities. Indeed a truly multipurpose pilot plant can be designed with enough room for expansion and possible future requirements.

2.7 Conclusions from Literature

The literature study firstly investigated supercritical fluids, determining what constitutes a supercritical fluid, its properties, and how it compares to classical solvents. Secondly the basics of hydrodynamics in standard packed countercurrent columns were established. It was found that hydrodynamics in packed columns are based on liquid films falling over packing elements

with countercurrent gaseous flow, and entails the measurement of liquid hold-up, pressure drop and flooding. Looking at the combination of the two fields, it was found that limited literature data on the topic is available. Existing research in the field showed that firstly, hydrodynamics under supercritical conditions are not readily predicted by models applicable at normal and vacuum pressures and secondly, that hydrodynamics under supercritical conditions are not fundamentally different from atmospheric hydrodynamics.

Several shortcomings were identified in literature and are summarised as follows:

- Previous studies use systems where significant solubility is possible, causing mass transfer to become an issue.
- Very little work has been performed on random packings and with no studies considering modern random packings.
- The effect of column diameter on hydrodynamics under supercritical conditions have not been investigated, even though wall effects should be significant.
- No columns below 25 mm inner diameter, $Ø_I$, have been investigated.
- Only CO_2 has been used as supercritical fluid in previous hydrodynamic studies.

Concerning the semi-empirical correlations proposed a few problems were also identified:

- The models have only been proven for a few packings at a very limited range of fluid properties, sometimes with dubious fits of the presented data.
- Very limited empirical constants are available and only for limited property ranges.
- No universal flooding correlation is available.
- No investigation to the effect of other elevated properties of supercritical fluids, such as viscosity or surface tension, on column hydrodynamics has been done.

The lack of data and shortcomings in literature force industry to rely on pilot plant studies for data, decreasing the attractiveness of the technology. Pilot plant studies are in turn also complicated, due to the lack of correlations to provide an initial guess of the flooding point, loading point and operating conditions. This leads to a time consuming, expensive, iterative process required to gather data. It also causes difficulty in differentiating between hydrodynamic, mass transfer and thermodynamic effects in a particular system.

In order to remedy the shortcomings in literature supercritical hydrodynamic pilot plant data is to be collected and investigated. As no pilot plant capable of measuring hydrodynamics under supercritical conditions was available at the time, an investigation was made into possible alternatives, including retrofitting existing pilot plants, purchasing a new pilot plant, or building a new plant in-house. It was found that building a new plant in-house, in conjunction with deconstructing an obsolete pilot plant for parts, yielded the best solution.

3. Aims, Objectives and Scope

3.1 Introduction

In the preceding chapter the need for supercritical hydrodynamic data was identified and shortcomings in literature discussed. To remedy the shortcomings, and provide a practical solution to industry needs, the overarching goal of providing a better design basis for supercritical columns is identified. This can be done by establishing standard semi-empirical or empirical hydrodynamic models for random packed columns for a range of fluid properties. This is a very ambitious goal and beyond the scope of this project. This project does, however, aim to provide the required groundwork for a subsequent study fulfilling the overarching goal. This is done by establishing the equipment required to measure the required hydrodynamic data.

As currently available facilities could not measure hydrodynamic data it was decided to construct a new pilot plant (see Section 2.6). To make the construction of the new facility economically viable, an existing pilot plant was dismantled and salvaged and the major equipment reused. This existing plant was built in 1990 for Sasol by SITEC-Sieber and used by Nieuwoudt (9) for his doctoral studies. A description of the plant is available in Appendix A, A1.2. Sometime later Sasol donated the pilot plant to the Stellenbosch University, Department of Process Engineering, and it was subsequently used by Schwarz (22) for her doctoral studies. Since then the pilot plant has become outdated, cramped and unused, meriting its dismantling and salvage. All of the major equipment, including pumps, oil heaters, refrigeration, heat exchangers, vessels and columns were salvaged from this plant and reused in the construction of the new pilot plant. This section contains the detailed aims, objectives, scope, and limitations of the construction and experimental verification of the pilot plant.

3.2 Aims and Objectives

The aim of this project is divided into two parts. Firstly, the aim of establishing a supercritical pilot plant and secondly, to prove that the pilot plant can deliver reliable hydrodynamic data, through the experimental measurement of supercritical hydrodynamic data. The aims will be discussed separately in the subsections below.

3.2.1 Aims Relating to the Construction of the Supercritical Pilot Plant

To achieve the first aim of establishing a new pilot plant, the following steps are required:

- Dismantling and salvaging the old SITEC-Sieber pilot plant to provide components for the new plant.
- Design and construction of a suitable pilot plant.
- Testing and validation of the completed pilot plant.

It is not often in research where the luxury of building a custom pilot plant presents itself and the pilot plant was carefully planned to meet not only the needs of hydrodynamic studies, but also that of possible future work. Future work, in this case, includes studies concerned with extraction or further hydrodynamics. Additionally, future work may require addition to, or modification of the pilot plant. Keeping this in mind the plant is designed with the following design objectives. Firstly, for the requirements directly relevant to this study:

- The liquid hold-up, pressure drop and flooding in a packed column under supercritical conditions should be measured accurately.
- A wide range of liquid and supercritical fluid phase flow rates should be available, all of which need to be quantified.
- A wide range of liquids with different fluid properties should be processable.
- All the relevant data should be logged electronically to eliminate the human factor in experimental readings.

Secondly, more general design objectives were:

- A maximum column working pressure of 300 bar, being the maximum pressure as inherited from the dismantled pilot plant and its equipment design limits.
- A maximum working temperature of 200°C. (This is also a limitation of the existing equipment, specifically the oil heaters.)
- The pilot plant must be able to handle different supercritical fluids, including possibly flammable gases such as propane and ethane.
- The pilot plant should be easy to expand on and add to.
- A control and logging system are to be set up for the pilot plant.
- All components must be easily accessible for cleaning and maintenance.
- The pilot plant should be safe in design and operation.
- User friendliness will be ideal.

Adhering to these objectives should provide a pilot plant with a long service lifetime with a diverse range of capabilities and possible research focuses.

3.2.2 Aims Relating to Supercritical Hydrodynamic Measurements

In order to meet the secondary aim of this project the pilot plant must be able to measure liquid hold-up, pressure drop and flooding of a packed column under supercritical conditions. The planning and execution of experiments should be directed towards this objective. The goals set for the experimental section of this study are:

- Select suitable packings.
- Select an appropriate supercritical fluid for experiments.
- Identify liquids that have no or negligible mutual solubility with the selected supercritical phase.
- Select a liquid to use in initial hydrodynamic experiments.
- If required, determine the solubility of CO_2 in selected liquid phases.
- Establish the loading and flooding points for selected systems.
- For selected systems, measure the:
    - Pressure drop,
    - Flooding,
    - Liquid hold-up,
    - and, if possible, entrainment.
- Compare results with existing data and correlations.

These goals tie in with the overarching goal to improve fundamental knowledge of hydrodynamic behaviour in packed columns using supercritical solvents, which was identified as a shortcoming in the literature review (specifically Section 2.5).

3.3 Scope and Limitations

The overall scope of this study was to establish a supercritical pilot plant and accurately measure supercritical hydrodynamic data. Various limitations define the scope of the construction and operation of the pilot plant. This in turn limits and shapes the experimental work, which moreover has its own limitations and subsequent scope. The scope and limitations for each main project aim will be discussed separately in the following subsections, followed by scope exclusions.

3.3.1 Pilot Plant Scope and Limitations

Operating limits

As previously mentioned in Section 3.1, the supercritical plant is built using major components from an existing pilot plant. These components are the limiting factors in the design of the new pilot plant. Significant limitations inherited from the previous plant are:

- A maximum operating pressure of 300 bar.
- A maximum operating temperature of 200°C.
- A maximum solvent flow rate of 55 ℓ/h.
- A maximum liquid flow rate of 8 ℓ/h.

Another physical limitation to the system is the circulation and preparation of the supercritical solvent, which has to be a liquid for the piston pump to be able to pump it. This sets a maximum temperature for the gas feed section which is dependent on the selected solvent, as discussed in Appendix F, F.2. This warrants the need of a refrigeration system, which is also transferred and modified from the old pilot plant.

Materials of Construction

Due to the system's high pressure, temperature, and possible future use of organic components which could be corrosive or dissolvent, 316 stainless steel high pressure tubing and fittings by Autoclave Engineers Inc. was used for all process tubing. The existing vessels and components salvaged from the old pilot plant are also constructed of stainless steel. Existing sight glasses on the solvent buffer level are made out of high pressure borosilicate glass while the sight glasses and level indicators on the column and separator are made out of clear sapphire. All the seals in the system are made out of polytetrafluoroethylene (PTFE), as rubber seals are affected by supercritical solvents. Exact tubing and component selections with regard to the high pressure limits are discussed in Section 4.4.3.

For the heating system, standard copper tubing and Swagelok fittings were selected. As far as possible, heating pipes were fitted as jacketing tubes over the high pressure process lines, creating an improvised double pipe heat exchanger. Where this was not possible the heating tubes were installed as tracing on the process lines and the contact area increased with heating paste. Copper tubing possesses excellent heat transfer properties, is corrosion resistant and is easily workable, making it ideal for this application. To safely and securely apply the copper tubing Swagelok brass fittings are used. The Swagelok system a double ferrule system that easily and securely seals.

The frame of the pilot plant was constructed from mild steel square tubing, square hollow beams and non-slip metal flooring sheets. This provided a cheap way of constructing a very sturdy, roomy structure to house the plant components. The frame design can be seen in Section 4.2.3. The mild steel is easily coated with enamel paints to create a protective layer and aesthetically blend in with existing facilities.

Safety

Safety is an important factor in any work of this scope and extreme process conditions. Precautions must be made when laying out the plant and selecting electronic devices and sensors. The properties of the fluid and solvents also need to be taken into account.

The safety of the pilot plant will be covered in more detail in Section 4.4, which includes a Hazard and Operability Study (HAZOP) and a general overview of the main risks and how they were mitigated.

3.3.2 Experimental Scope and Limitations

As discussed in the literature section, specifically Section 2.3.5, mass transfer must be limited during fundamental hydrodynamic investigations. This limits the selection of the supercritical solvent and liquid component to a binary system with no or low mutual solubility. Further, both must be safe to use and, if possible, of low cost.

The liquid has to have an acceptable viscosity to be pumpable. Ideally the properties of the selected fluid should compare well to typical industrial fluid solutions used in supercritical extractions. A range of fluids should be selected to provide a range of liquid properties to provide a full hydrodynamic overview.

The supercritical solvent must be relevant to industry use with the critical point falling within the limits of the pilot plant.

3.3.3 Scope Exclusions

The following goals fall outside the scope of this project and is not under investigation:

- This project does not aim to measure a full range of hydrodynamic systems, but rather to prove a concept and its viability. The main focus of the project is to establish the pilot plant.
- The project does not aim to develop new correlations that predict hydrodynamics under supercritical conditions.

- The hydrodynamics of tray columns or columns with structured packing are not considered. Only randomly packed columns are to be investigated in this study. The pilot plant is however constructed in such a way that structured packing can be investigated in future.
- Only one supercritical solvent is considered, even though the pilot plant can handle other systems.
- Foaming of the liquid phase is not measured, as that would entail the installation of expensive additional sight glasses into the column. Furthermore, foaming has been reported to be negligible (13) at high pressures, decreasing the likelihood of this being a major effect.

4. Experimental Method, Design and Construction

In order to achieve the first aim of this study a pilot plant was designed and constructed. In this chapter the process flow and design is first conceptualized, after which a detailed design of the pilot plant is done. In concordance with the second aim of measuring hydrodynamic data, an experimental system consisting of a supercritical solvent, liquid and packing is selected. At the end of the chapter a description of the experimental method and measurement of hydrodynamic data is provided.

4.1 Process Concept

A basic process concept for a supercritical pilot plant was assembled using the design knowledge acquired from the pilot plants investigated in Section 2.6. A supercritical pilot plant typically consists of four sections, being the solvent, liquid, extractor and separator sections. A typical example of each of these process sections is described in the headings below, followed by a summary of the utilities required. A basic concept sketch showing the rudimentary process flow and the way the sections link together can be seen in Figure 4- 1.

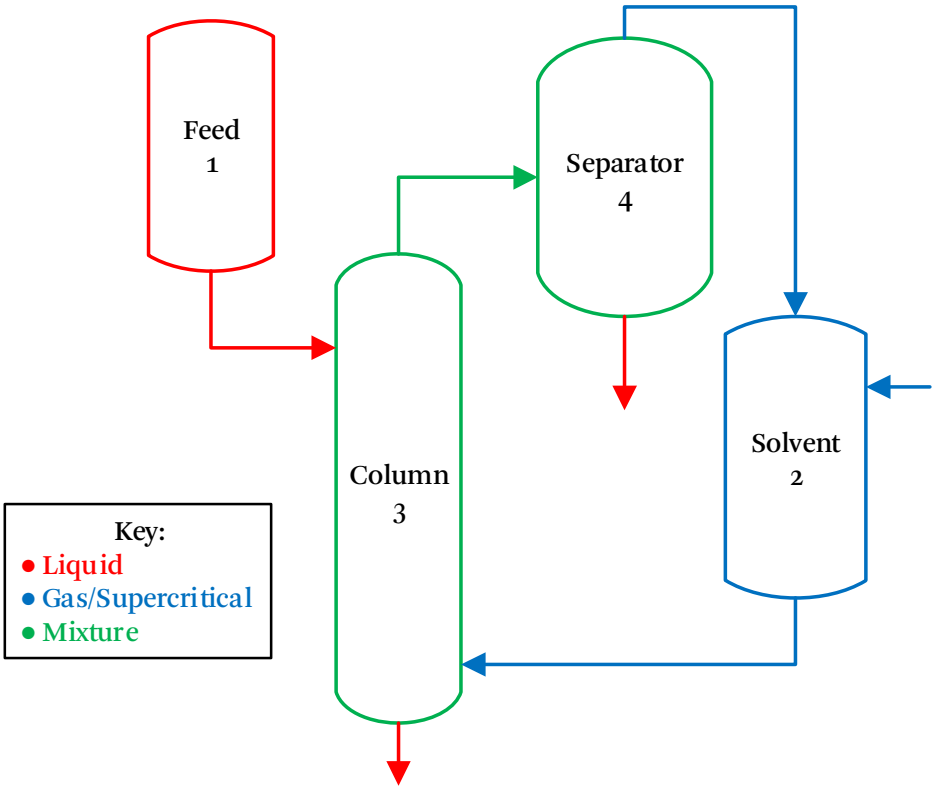


Figure 4- 1: A basic concept sketch for a supercritical pilot plant process.

4.1.1 Liquid Section

The feed section consists of a feed cylinder or vessel and one or more positive displacement pumps. During operation a semi-batch load of feed is placed into the feed cylinder. The cylinder and pump can be heated to ensure molten feed at the correct process temperature. From the feed cylinder the feed is pumped by the positive displacement pump to the column section.

4.1.2 Solvent Section

The solvent section consists of one or more solvent gas cylinder(s), a solvent buffer tank and positive displacement pump. Fresh solvent is loaded into the system from the solvent gas cylinder. The fresh solvent, along with gas phase solvent from the solvent recovery section, is cooled into a liquid phase by refrigeration coils or chilled heat exchangers. The liquefied solvent is in turn then stored in the solvent buffer tank. From the solvent buffer tank the liquid solvent passes through a further chiller before being pressurized in the positive displacement pump. The solvent is then reheated into the supercritical phase before entering the column.

4.1.3 Extractor Section

The column section consists of one or more columns and/or solid extraction units. Columns have middle and/or top liquid feed ports with the solvent from the solvent section fed at the bottom. Columns are packed with structured or random packing. Solid extractors are typically loaded batch wise with solid feedstock, with the solvent also pumped through from the bottom. The loaded solvent leaving the section is fed to the solvent recovery section. The liquid leaving the column can be recycled to the feed section or decanted at the bottom of the column.

4.1.4 Separator Section

The solvent recovery section contains a pressure control valve and one (or more) separator vessels. The top product from the column is heated to avoid precipitation and fed to the control valve. The control valve can either be a regulating valve or have an on/off type control. The low pressure top product is then fed to the separator vessel where the liquid is allowed to settle by gravity. The gaseous solvent then passes through a filter and is fed back to the solvent section. Liquid product is stored in the separator or decanted in a batch wise fashion.

4.1.5 Utilities

Basic utilities required include heating and cooling. Heating is used to maintain supercritical temperatures and ensure uniform properties in the column. Cooling is used to liquefy the solvent before pumping. Pressurized air is used for pneumatic control, where required.

4.1.6 Hydrodynamic Measurements

In order to measure hydrodynamic data the pressure drop over the packing and the liquid hold-up in the column is required. The pressure drop can be measured using a differential pressure cell or DP cell. To measure the liquid hold-up the column must have sufficient room in the bottom for the liquid to settle. Flooding can possibly be investigated by monitoring the liquid level above the packing, which can be done by using a level sensor.

4.2 Detailed Design

The detailed design consists of a set of P&IDs (Process and Instrumentation Diagrams), the procedure followed on integrating the existing equipment from the old pilot plant and a plant layout. This is followed by and in-depth discussion of the selection of various systems such as the column packing, liquid-solvent systems and sensors.

4.2.1 Process & Instrumentation Diagram

The process and instrumentation diagrams are split into four pages, each representing a section of a typical supercritical pilot plant, as discussed in Section 4.1. A rough overview can be seen in Figure 4- 2.

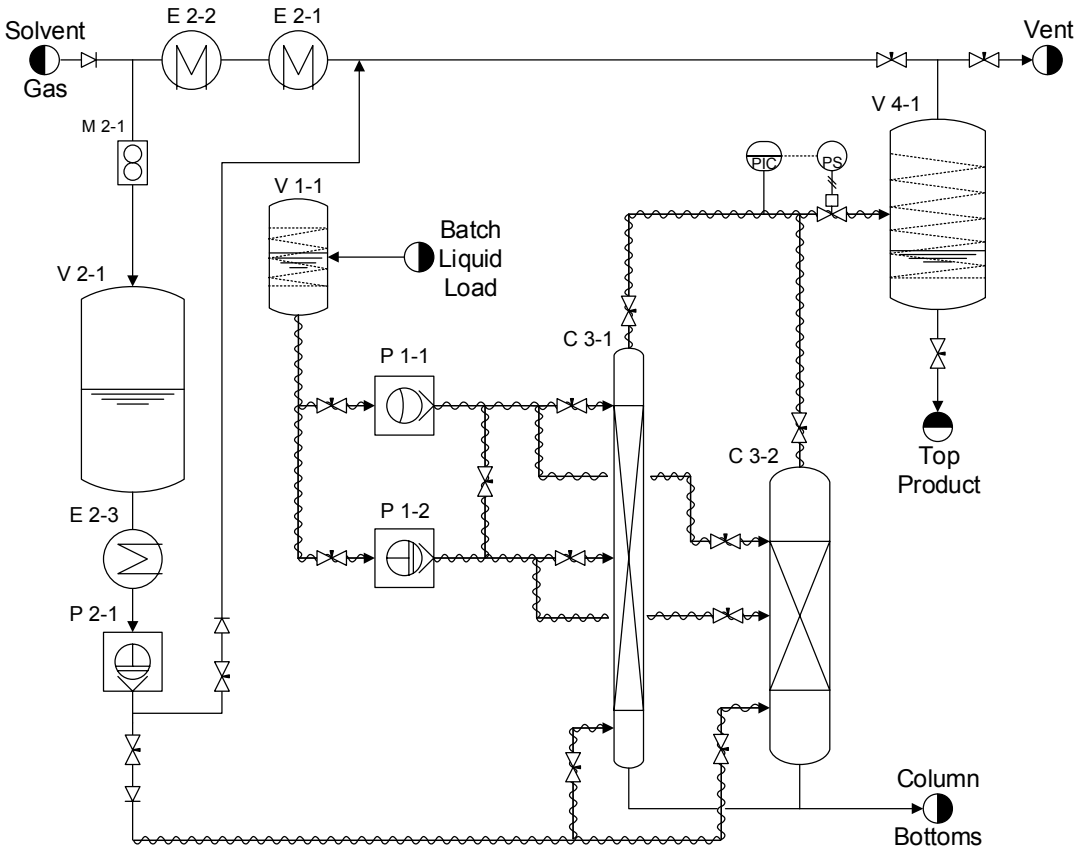


Figure 4- 2: Overview of the newly constructed pilot plant units.

The detailed P&IDs for each section can be seen in Figures 3–3 to 3–6 after Section 4.2.3. All subsequent referrals to equipment numbers will refer to the equipment as identified in the P&IDs.

4.2.2 Available Existing Process Equipment and Integration

The required major pieces of equipment had to be salvaged from an existing pilot plant to save costs. The following list summarises the reused equipment with their corresponding equipment numbers, as used in the new pilot plant:

- P 1-1: 2 ℓ/h Lewa diaphragm pump – used for liquid feed pumping.
- P 1-2: 8 ℓ/h Lewa positive displacement pump – used for liquid feed pumping.
- P 2-1: 55 ℓ/h Lewa diaphragm pump – used for solvent pressurisation and pumping.
- V1-1: 2 ℓ feed vessel.
- V 2-1: 10 ℓ solvent buffer tank.
- C 3-1: 4.3 m high, 17 mm $Ø_I$ column.
- C 3-2: 2 m high, 38 mm $Ø_I$ column with sight glasses and level sensors.
- V 4-1: 11 ℓ separator vessel with a packed mesh demister, carbon filter, sight glasses and level sensor.
- R1: Custom refrigeration system for cooling duty.
- H1 and H2: Two 8 kW Tooltemp oil heaters for heating duty.
- E x-x: Double walled heat exchangers for cooling and heating.
- M 2-1: Micro Motion mass flow meter.
- PIC 4-1: A high pressure sensor.
- PI x-x: All pressure gauges. Three gauges with a maximum of 300 bar and one of 100 bar.
- T x-x: All the temperature sensors, being J type thermocouples.
- LE x-x: Two Liquiphant DL 17 Z liquid level sensors.
- L x-x: Three Incatronic optical level sensors with high pressure sapphire cone process connections.

All of the equipment was thoroughly cleaned and serviced before installation into the new pilot plant. Most of the components could be transferred to the new pilot plant without modification, except for the pumps, refrigeration and heating systems. The pump hydraulic and gearbox oils were replaced and diaphragms were inspected and cleaned.

The refrigeration system, R1, was a customized system and had to be rebuilt to accommodate the new pilot plant. To ensure the refrigeration system conforms to future regulations it was

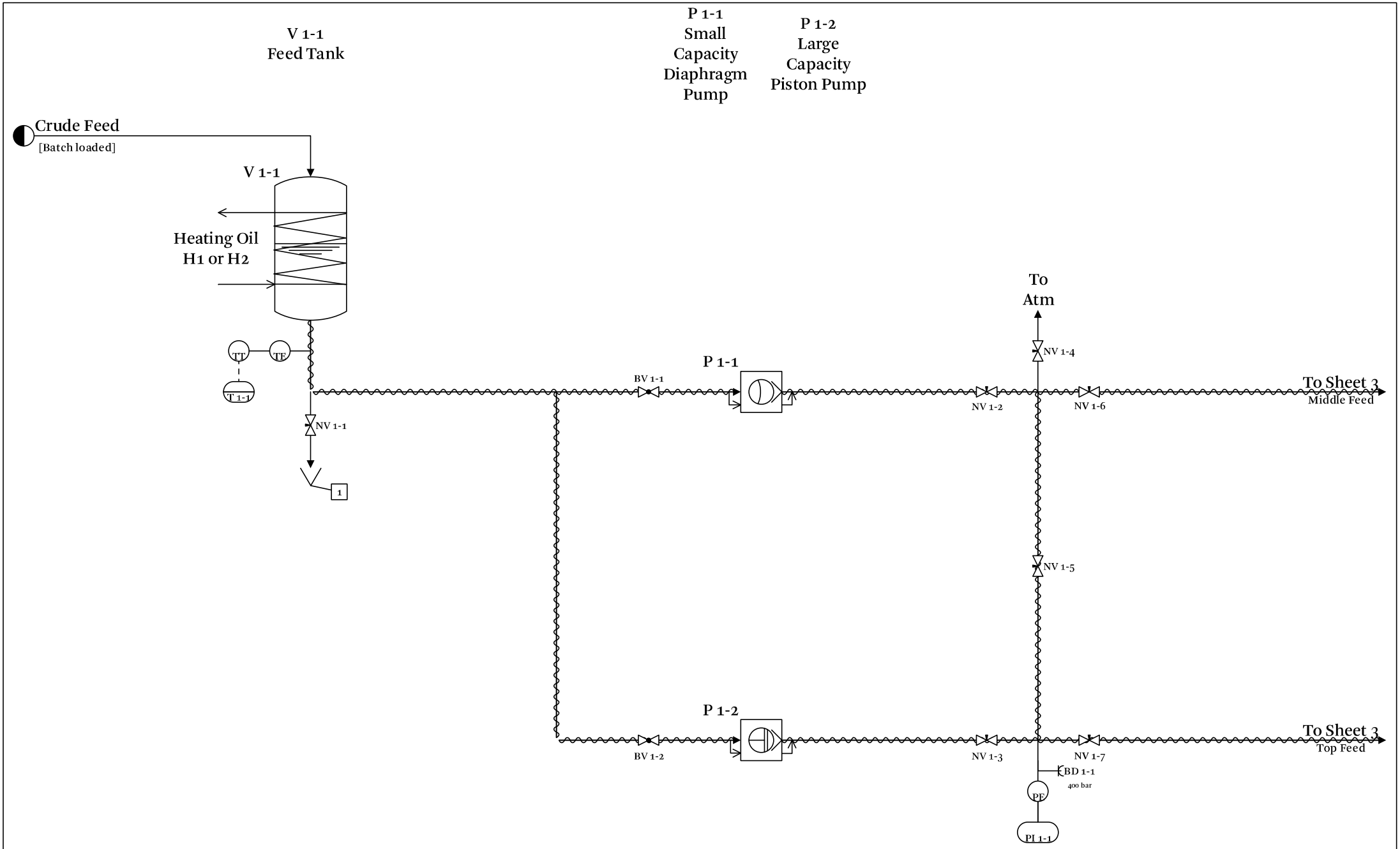
retrofitted to use refrigerant R507 in place of the original CFC gas, R22. The piping and gas conversion was performed with the help of the company, Azure Refrigeration. The P&ID of the rebuilt refrigeration system can be seen in Figure 4- 7, with more details to the rebuilding and commissioning in Appendix C, C.5.1.

The oil heaters, H1 and H2, were flushed and serviced and faulty key electrical components were replaced. In order to provide sufficient heat duty to the system process lines, copper tubing carrying the heating oil was either applied as double walled exchangers or tracing, as discussed in Section 3.3.1. A P&ID of the heating system can be seen in Figure 4- 8. After construction the heaters were filled with Dowtherm A heating oil to serve as heating medium. The commissioning of the heating system is described in Appendix C, C.5.1. The MSDS for Dowtherm A can be seen in Appendix B, B.1.

4.2.3 Plant Layout

In order to accommodate the new pilot plant a frame was built from mild steel, as discussed in Section 3.3.1. The frame was designed to fit into the area available, provide easy access to all of the process units and leave room for future expansion. Critical welds on the frame were visually checked for quality and their strength calculated using the BS 5950 standard (calculations available in plant manual). The frame can be seen in Figure 4- 9, followed by a 3D plant layout of the major equipment in Figure 4- 10. The piping layout was also done using graphical software, but is omitted for the sake of brevity and ease of interpretation.

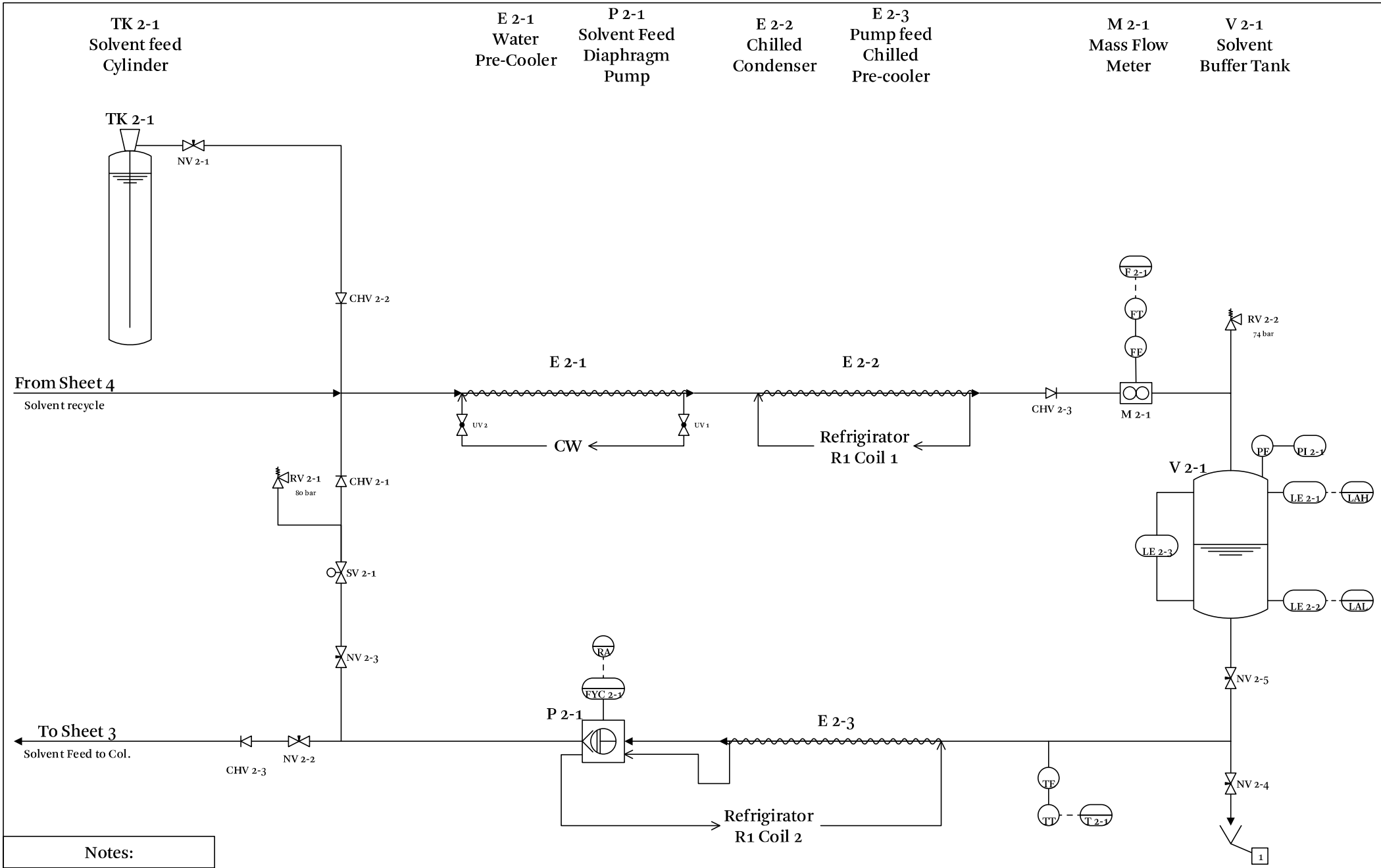
The final plant, without insulation can be viewed in Figure 4- 11.



Notes:
BD – Burst Disk BV – Ball Valve NV – Needle Valve 1: Drain Point

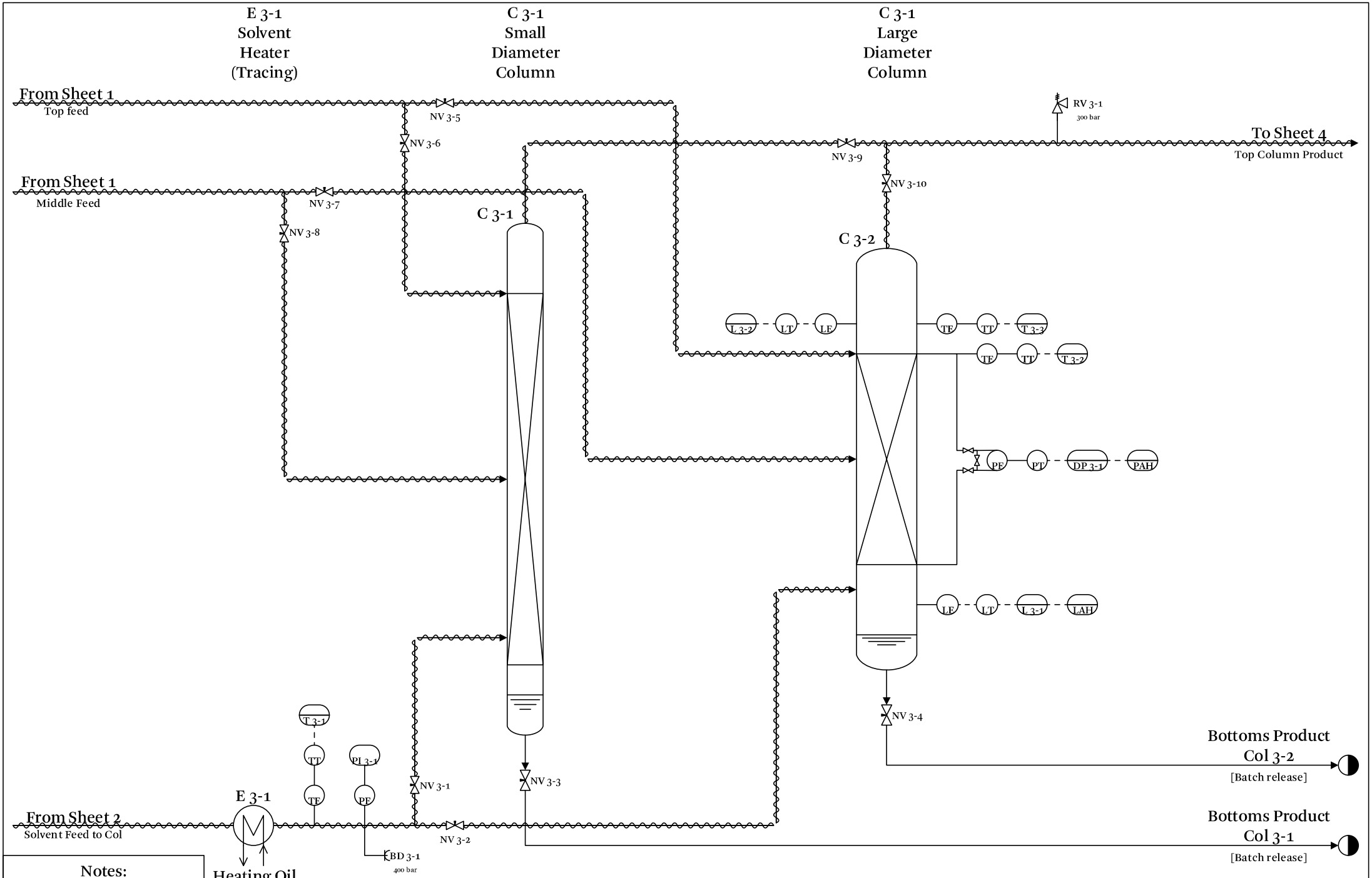
All lines and vessels are traced from H1 or H2. Selectable at TTV 1 and TTV 2

Process P&ID Section 1 – Liquid Feed Section	Figure	Rev
	4-3	4



Notes:
NV – Needle Valve CHV – Check Valve SV – Regulator Valve RV – Relief Valve UV – Utility Valve 1: Drain Point

Process P&ID Section 2 – Solvent Preparation & Recovery	Figure	Rev
	4-4	4

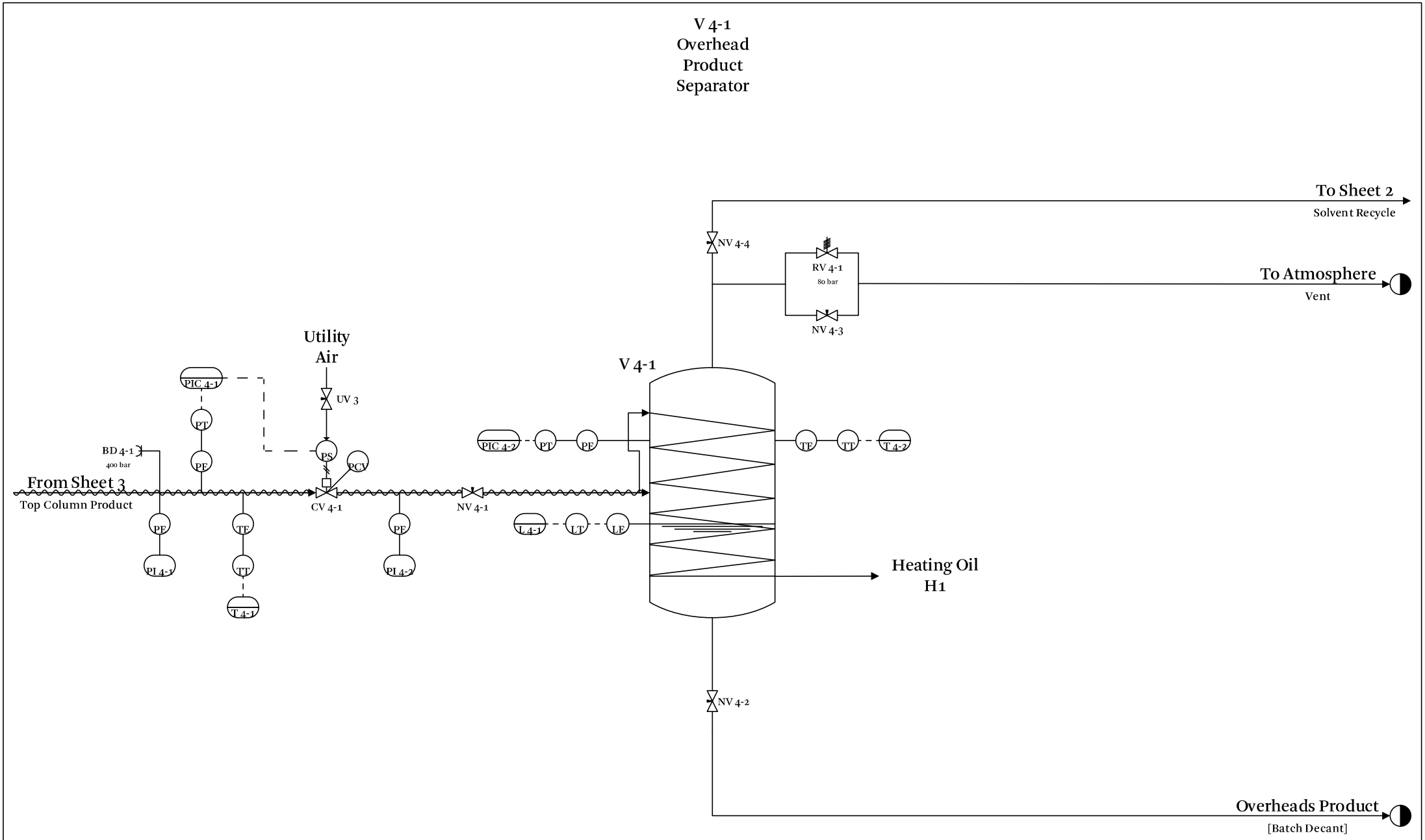


Notes:

BD – Burst Disk
NV – Needle Valve
RV – Relief Valve

Top column product traced from H1.
Remaining lines and columns traced from H2.

Process P&ID Section 3 – Columns Section	Figure	Rev
	4-5	4



Notes:
BD – Burst Disk CV – Control Valve NV – Needle Valve RV – Relief Valve UV – Utility Valve

Tracing for tank and incoming line from H1 – high temp.

	Figure	Rev
Process P&ID Section 4 – Separator	4-6	4

1	Compressor	5	Coil 1: Process Evaporator	9	Danfoss Solenoid Valve	13	(Danfoss) Thermal Expansion Valve
2	Oil Separator	6	Coil 2: Pump Evaoprator	10	Danfoss Solenoid Valve	14	(Danfoss) Thermal Expansion Valve
3	Condenser	7	Liquid Separator	11	Hot Gas Bypass Valve CPHE (ALCO)	15	(Danfoss) Evaporation Regulator Valve
4	Liquid Collector	8	Danfoss Solenoid Valve	12	Liquid/Liquid Injector Valve	16	(Danfoss) Evaporation Regulator Valve

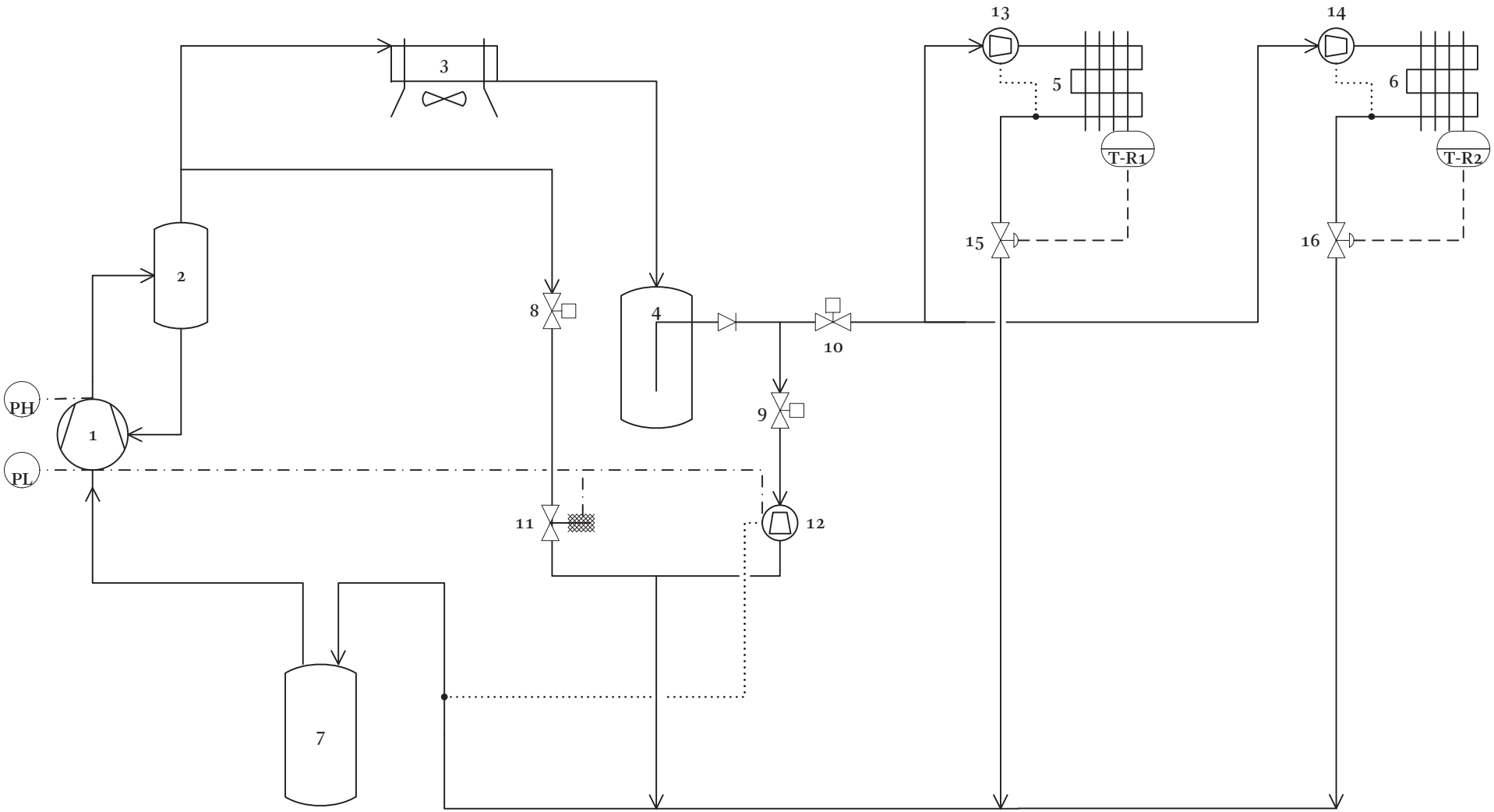
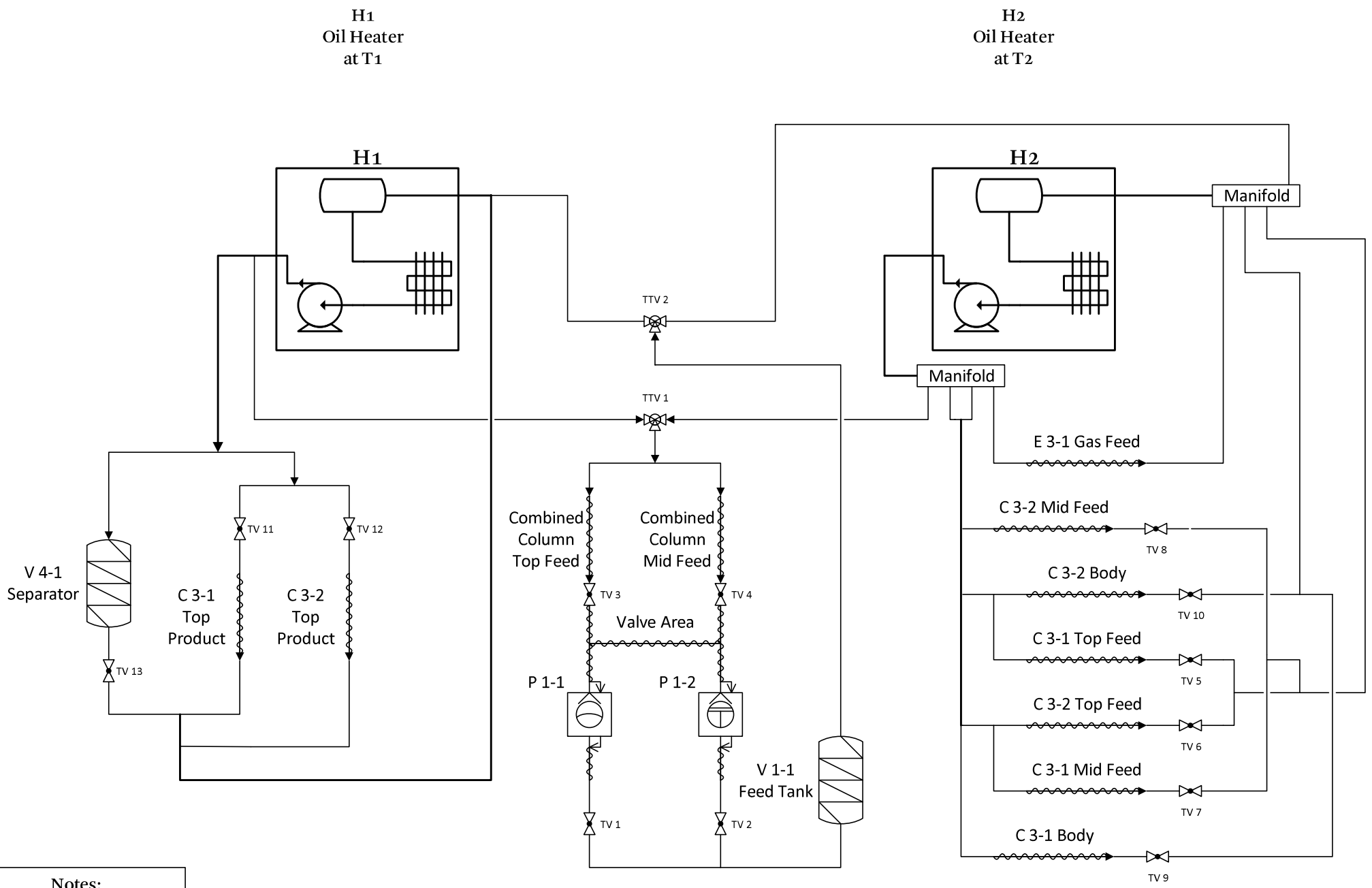


	Figure	Rev
Utility P&ID - Refrigeration system R1	4-7	3

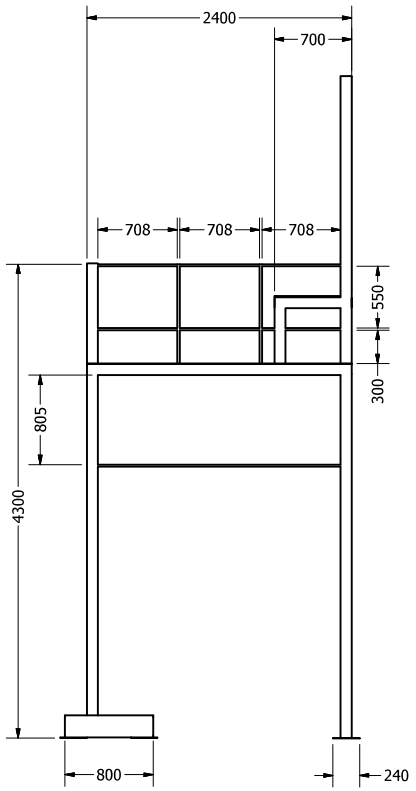


Notes:
— – 3/4" Tubing
— – 3/8" Tubing
TV – Temperature Valve
TTV – 3-way Temperature Valve

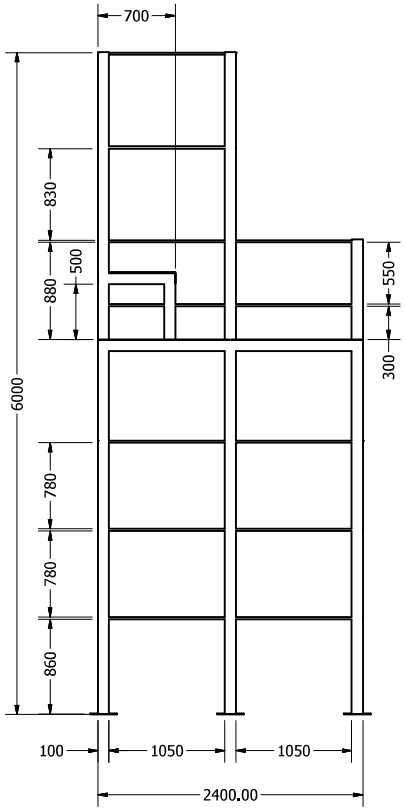
For normal operation H1 at T1 and H2 at T2. T1 > T2.

Utility P&ID – Oil Heaters H1 and H2	Figure	Rev
	4-8	2

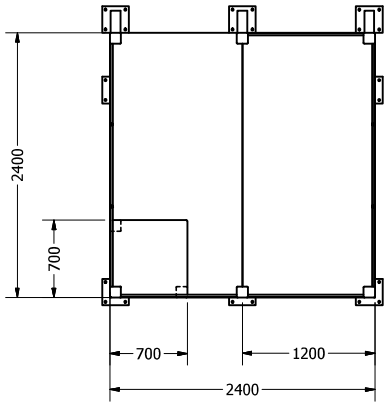
Left View

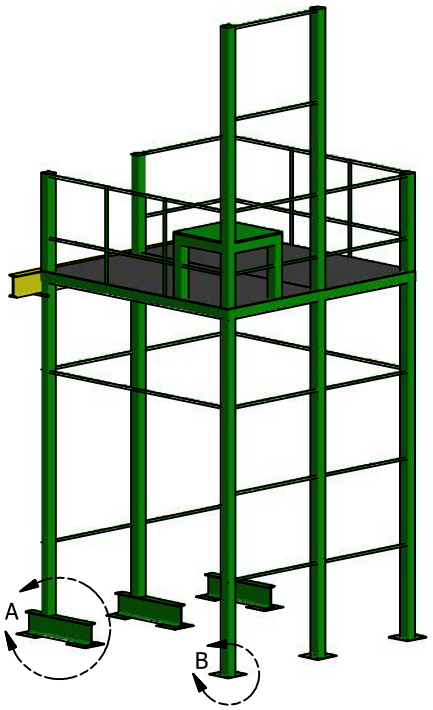


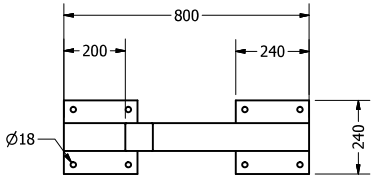
Front View



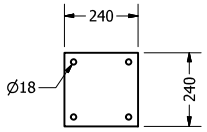
Top View







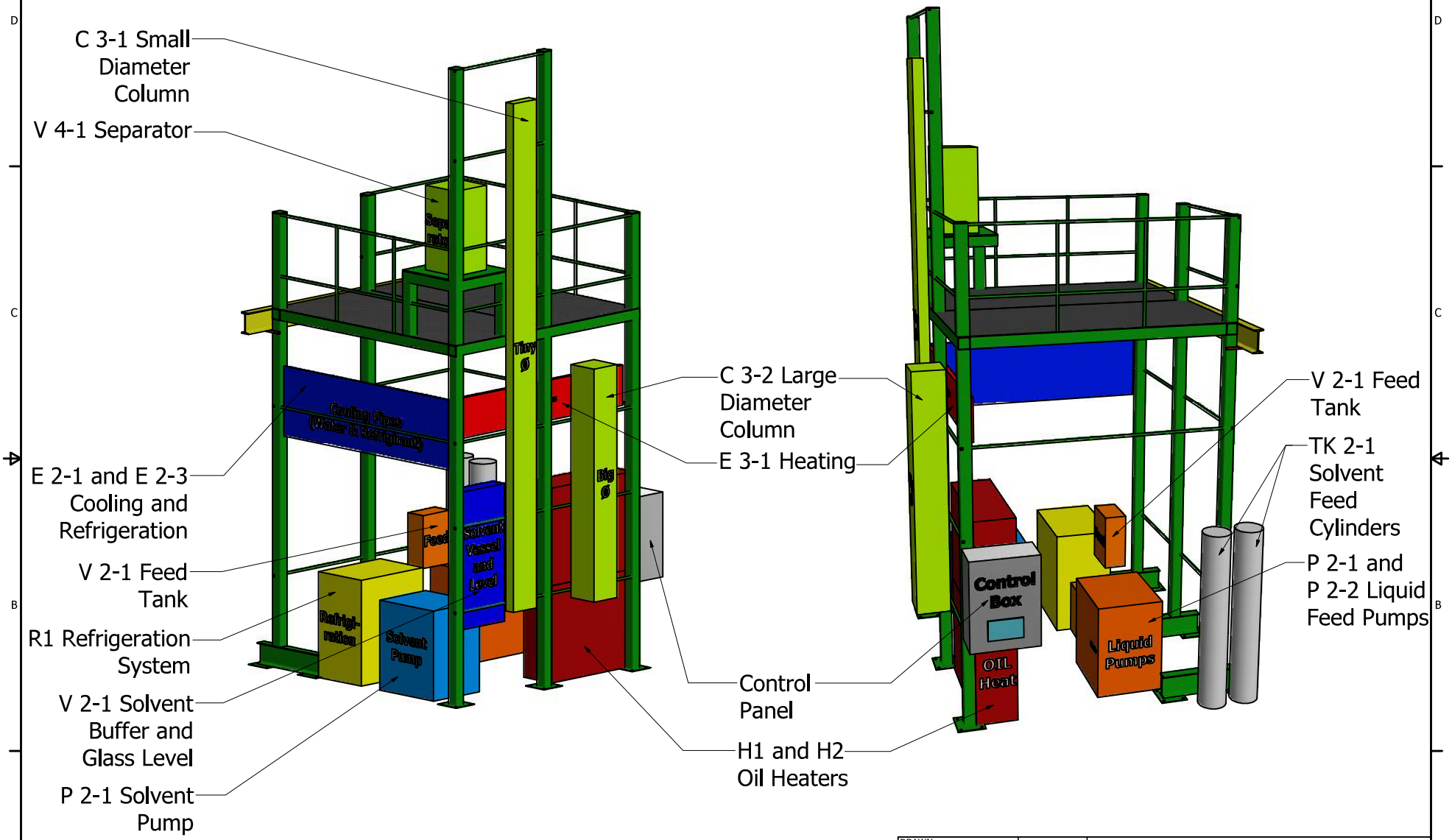
Detail A



Detail B

PARTS LIST		
QTY	PART NUMBER	DESCRIPTION
8 times 6000 mm	25 x 25 x 2 mm tubing	Cold formed welded structural hollow sections of non-alloy and fine grain structural steel
8 times 6000 mm	100 x 100 x 6 mm tubing	Mild structural steel square tubing
2 times 2400 x 1200 x 3 mm	3 mm checkered plate	Hot rolled mild steel flooring sheets with oval grip pattern
2400 mm	100 x 200 mm I beam	Hot rolled I-beam
700 x 700 x 12 mm	12 mm plate steel with 100 x 100 mm cutout	Mild structural steel plate
9 times 240 x 240 x 5 mm	5mm plate steel	Mild structural steel plate

DRAWN H Franken	2013/12/16	
CHECKED	Y	
QA	Y	TITLE: Figure 4-9: Pilot Plant Frame
MFG		
APPROVED	Y	
SIZE C	DWG NO Drawings	REV 3
SCALE	SHEET 1 OF 2	



DRAWN H Franken	2013/12/16			
CHECKED	Y	TITLE Figure 4-10: Pilot Plant Unit Layout		
QA	Y			
MFG				
APPROVED	Y			
		SIZE C	DWG NO Drawings	REV 3
		SCALE	SHEET 2 OF 2	

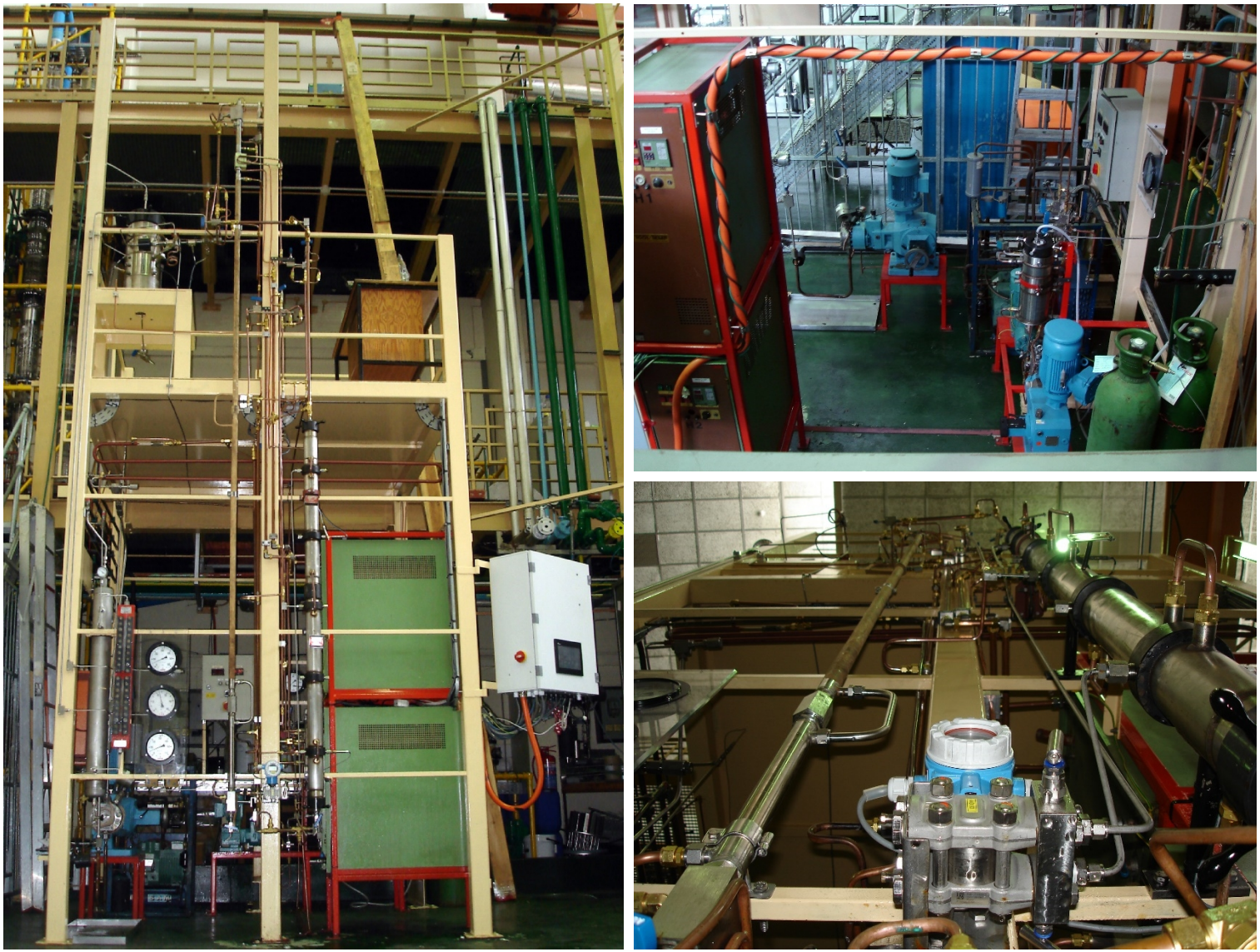


Figure 4- 11: Photos of the pilot plant. From left moving clockwise: A full frontal view; Inside of the pilot plant; The two columns and DP Cell.

4.2.4 Sensor Placement and Accuracy

As stated in Section 3.2.2, the measurement of liquid hold-up, pressure drop, flooding and, if possible, entrainment is one of the aims of the study. These measurements are to be made at known liquid and supercritical phase flow rates, pressures and temperatures. To achieve this aim, and to control the pilot plant setup safely, an assortment of sensors is required. This includes temperature probes, pressure gauges and transducers, level sensors, a mass flow meter and a differential pressure cell or DP cell. In this section the accuracy of each sensor type is briefly discussed, followed finally by the calibration and scaling of the sensors in the PLC. Detailed individual sensor placement discussions can be found in Appendix C, C.1, followed by detailed calibration methods in Appendix C, C.2.

Temperature Sensors

The temperature sensors are all existing J type thermocouples salvaged from the existing pilot plant (see Section 4.2.2). J type thermocouples are used for temperatures between -40°C and 750°C with a reported accuracy of $\pm$1.5°C. All thermocouples were calibrated with an offset value in the PLC system to ensure accuracy.

Pressure Gauges and Sensors

Several Bourdon tube gauges from SITECH-Sieber were recovered from the original pilot plant (see Section 4.2.2). A total of four gauges are reused with three gauges having a maximum pressure of 600 bar, accuracy of $\pm$2.5 bar, and one of 100 bar, accuracy $\pm$1 bar. The gauges have been compared to known pressures during pressure testing and have shown to provide good readings. An additional stainless steel bourdon tube gauge, maximum pressure 160 bar, was procured from Wika Instruments and installed on the solvent buffer tank.

Two pressure transducers are used in the pilot plant, one an existing transducer of unknown make and one purchased from Wika Instruments. The first transducer has a maximum working pressure of 500 bar and is reported in the work of Schwarz (22) as having an accuracy of $\pm$1.0 bar. The second transducer is a type A-10 Wika transducer and has a range of 100 bar with a reported accuracy of $\pm$1.0 bar.

Level Indicators

Two Liquiphant DL vibronic level switches from Endress+Hauser were salvaged from the existing pilot plant (see Section 4.2.2). These sensors indicate liquid levels with an accuracy of ±2 mm.

A type 68/40.6 borosilicate glass reflex level gauge, built by F. Vaihinger GmbH & Co., was transferred from the old pilot plant to indicate the liquid level over the solvent buffer vessel. The gauge has a maximum working pressure and temperature of 100 bar and 120°C.

Three optical level switches constructed by Incatronic were salvaged. These sensors can measure liquid level changes in high pressure environments using a sapphire cone. This method can pinpoint the liquid level with a repeatability of ±0.5 mm.

Mass Flow Meter

A single mass flow meter is installed after the chilled condenser, E 2-2, to measure the flow of solvent from the separator and, indirectly, from the columns. The mass flow meter is composed of two units, both manufactured by Micro Motion, being a D12 flow sensor and a RFT 9729 remote flow transmitter.

The remote flow transmitter receives data from the flow sensor, after which it filters the data and converts it into a flow rate using a calibration factor. The flow transmitter also incorporates a temperature correction factor calculated from the temperature received from the flow sensor. The temperature compensation has a resolution of 0.1°C and a range of -250°C to 400°C. The accuracy of the total flow assembly is reported as ±0.2% of the current rate plus ±0.01% of the sensor upper range limit. To determine total accuracy of the sensor the upper range limit is required. Unfortunately no manual could be sourced for the mass flow meter.

DP Cell

As the existing pilot plant did not have the capacity to measure pressure drop over the column, a sensor had to be sized and selected. The sensor would have to conform to the following specifications:

- Maximum operating pressure of 300 bar.
- Maximum temperature of 200°C.
- Capable of measuring pressure drops of up to 50 kPa. This value is the result of an estimation from literature (13; 14).
- High accuracy of measurement.

An Endress+Hauser Deltabar S PMD75 was selected, being the only solution found that could achieve the above specifications. Even though the sensor only has a maximum operating temperature of 120°C, this is overcome by connecting the sensor to the column with capillaries of sufficient length to dissipate the excess heat.

The DP cell reports an accuracy of 0.075% of its range of 50 kPa, being an accuracy of 37.5 Pa.

PLC Sensor Scaling and Calibration

Accurate calibration and scaling of sensors avoid unnecessary error in experimental readings. All the sensor outputs are scaled with respect to their operating ranges, adjusted with offset values from calibration and then averaged over 10 ms before being displayed on and logged by the HMI system.

Both pressure and temperature sensors were calibrated with an offset value in the controller. The offset value was obtained by comparison with a known value during calibration tests. Liquid levels were tested using submersion tests. More details regarding the sensor scaling and calibration tests can be seen in Appendix C, C.1, with typical calibration values in Section C.1.4.

4.2.5 Control System and Data Acquisition

To control and monitor the pilot plant properly, an appropriate control system was selected and installed. An Ethernet PLC control system was deemed the best solution. After consulting several providers, Ateka Automation was contracted to construct a control panel. The panel includes a main switch, circuit breakers, contactors for major equipment, a Delta Electronics PLC system with touch screen HMI interface and the panel wiring. In this section the PLC, HMI and alarm control systems are discussed.

PLC, Programming and Control Loops

A PLC or 'Programmable Logic Controller' is a digital computer used to control, monitor and/or automate a process. PLCs can handle multiple inputs and outputs, with a modular design for easy expansion, while providing a robust industrial control solution.

The core PLC ladder programming was done by Ateka Automation with further modifications performed using WPLSoft (91). Programming done by Ateka Automation included the pressure control loop, which uses pressure sensor PIC 4-1 to control valve CV 4- 1 with an on/off control philosophy, and all of the alarm and calibration systems.

Several additional features were added onto the original core programming, including a start-up sequence, partial solvent bypass sequence, control valve alarm cut-out state, control valve

manual override and an emergency stop button. Each of these modifications will be discussed individually in the following paragraphs.

The start-up sequence allows the operator to bypass the low level alarm, LAL 2-2, on the solvent buffer tank on the gas feed section of the HMI. This allows the operator to load solvent without interference from alarms. The sequence further allows the operator the option to turn on the solvent pump, P 2-1, before the liquid level is reached in the buffer tank. If the operator does not turn on the pump, the solvent pump is automatically turned on after the level is reached. This allows the liquid solvent to circulate through the bypass loop and accelerate further solvent precipitation.

The partial bypass system is used when a very low solvent flow rate is desired. This allows the operator to reduce the flow to the column by opening the solvent bypass loop and tuning regulator valve SV 2-1. The HMI then calculates the true solvent flow rate based on a set value defined by the operator. This mode is not particularly accurate, as it assumes the solvent flow rate from the condensers to be constant. As soon as the bypass is initiated the equilibrium of the system is disturbed and hence the flow from the condensers changes. This is why this sequence is only advised for very small solvent flow rates, where the effect on equilibrium will be negligible.

The control valve alarm cut-out state was added to define the on/off state of the control valve during an emergency shutdown triggered by either an alarm or the operator. The default state of the valve during an alarm is closed to avoid losses to the atmosphere. Scenarios may occur where the operator would prefer the column pressure to vent into the separator and, subsequently, to the atmosphere through pressure relief valves downstream. This might be the safer option during operation at extremely high pressure, avoiding a possible rupture because of pressure build-up.

A manual control valve override was added for the convenience of the operator. Although it is true that the control valve can be opened by changing the set point, the override function allows fast control as the changing of the set value takes time. This function is also handy while venting or cleaning the system, allowing the valve to be kept open.

To ensure safe operation, a digital emergency stop is incorporated into the PLC and HMI. This turns of all the pumps and may open the control valve, depending on the selection of the control valve cut-out state.

HMI system

The HMI or 'Human Machine Interface' provides the link between the PLC and the pilot plant operator. Further the HMI handles the scaling and logging of all the measured values from the PLC. The HMI 'Graphical User Interface' of GUI was designed and populated using DOPSoft (91). The GUI was designed to be intuitive, easy to understand and simple to navigate. The main screens of the GUI can be seen in Appendix D.

An Ethernet switch was installed in order to allow a laptop or personal computer to be used to control the pilot plant. In order to do this, the computer has to be connected to the HMI with the Ethernet cable provided. Ensure the computer has static IP, coded to 192.168.1.4, to ensure stable communications. The pilot plant can now be controlled through the computer using DOP eRemote (91). The Ethernet connection can also be used to download, alter and upload the HMI and PLC software and firmware.

Alarms

To ensure the safe operation of the pilot plant, alarms are set up on all the digital inputs. Alarms are set up differently for each reading with respect to the risk involved with the reading exceeding set limits. The implementation and reasoning behind each individual alarm is found in the HAZOP study in Section 4.4.1. Two alarm types were used. Firstly, a cut-out alarm that turns off the system and, secondly, a warning alarm for less critical events.

The pressure alarms are set up using a cut-out alarm. The alarm consists of two mechanisms controlled by an alarm and a cut-out set point. Firstly, if the value reaches the alarm value an operator specified time delay is used to turn off the system. This allows the system to recover from a momentary overshoot. Secondly, if the read value exceeds the cut-out value the PLC immediately turns off the system. Level, heater and refrigeration alarms operate on the same principle, only without the immediate cut-out value. This is because the level, heater and refrigeration alarm triggers only have an on/off state. The alarms and typical set values can be seen in Appendix D: Figure D- 7.

For the temperatures and mass flow alarms a less strict approach is followed, as there is no immediate serious risk when these values exceed their bounds. A warning alarm system is used and no provision is made for these alarms to turn off the pilot plant. Rather the alarm is of an informatory nature, warning the operator of anomalies in the system. A low and high warning value is set for each alarm, as can be seen in Appendix D: Figure D- 8.

4.2.6 Column Internals

As stated in Section 2.2, the column internals have a direct impact on the operability of a column. This makes the selection of column internals an important choice in experimental planning. As briefly discussed in Section 2.2.2 columns are traditionally divided into two types with respect to internals, namely tray columns and packed columns. Packed columns are then further divided into random and structured packed columns.

Packed columns tend to be better for high pressure applications, having a low pressure drop and large capacity. Further packed columns handle foaming better and are typically cheaper than tray column counterparts for the small diameter columns used in supercritical systems. Tray setups can be constructed for small diameter columns in the form of cartridge trays, but are not available as a standard option, implying very high custom construction costs.

Packing

As stated in the previous section, packing is divided into random and structured packing. There is also a third category, namely grids, but it is not of interest to this study as it is limited to heat transfer and washing applications (47).

In Section 2.5 it was identified that very little work has been done on random packings in supercritical fluid environments. Random packing, being significantly cheaper than structured packing for such small diameters, provides a better economic solution. Random packing is therefore the best option both in terms of cost and research applicability. To this end an array of random packings was procured for the new pilot plant. These packings and their properties are summarised in Table 4- 1. Borosilicate glass Raschig rings were also considered for this study, but was not included in procurement. Only the ¼" Dixon rings are to be investigated in this study, due to time constraints, with the remainder reserved for the follow up study.

Demister

The large diameter column, C3-2, has a permanent demister at the top of the column made from sintered metal. The demister will hamper overall entrainment and hence liquid leaving the column due to entrainment is unlikely. Local entrainment in the column is however still possible. This column will be used for initial experiments, meaning that any entrainment measured at the column overheads during experiments should be unlikely.

The small diameter column, C 3-1, has no demister system and entrainment measurement is possible.

Table 4- 1: Selected packing and their respective properties.

Packing	Profile	Material	Size	Void Fraction	Surface area/vol (m^2/m^3)
Propak		SS316 punched ribbon	0.16" or 4.06 mm	94 %	1890
		SS316 punched ribbon	0.24" or 6.10 mm	96 %	1220
Dixon rings		SS316 60x60 mesh	1/8" or 3.18 mm	91 %	2378
		SS316 100x100 mesh	1/4" or 6.35 mm	91 %	900
Raschig		Borosilicate glass	4 mm	87-91 %	1000-630
		Borosilicate glass	6 mm	87-91 %	1000-630

4.2.7 Testing Fluids

As the aim of the study is to investigate hydrodynamics, the effect of mass transfer between phases is to be minimized. As discussed in Section 2.3.5, mass transfer can cause significant changes in mass flow rate and fluid properties, affecting hydrodynamics. Finding suitable liquid and supercritical solvent components is challenging as most supercritical solvents readily dissolve most organic compounds to some degree. A further complicating factor is the mutual solubility of systems, or in other words, the tendency of the supercritical solvent to dissolve into the liquid phase.

Ideally a wide range of liquid/supercritical fluid systems should be investigated, but due to time constraints this study will research possible systems and select one for experimentation.

Supercritical Fluid Phase

As a virtually endless number of possible combinations can be formulated, the scope is limited to using CO_2 as the supercritical fluid of choice. CO_2 has a critical point of 304.25K (31.1°C) and 73.8 bar, being able to operate at almost ambient temperatures and relatively 'low' pressure. CO_2 is inexpensive, safe, and environmentally friendly and does not react with process components. Indeed CO_2 can be seen as the most popular supercritical solvent (8), with wide use in industry. The wide application of CO_2 increases the value and applicability of the hydrodynamics measured. An MSDS sheet for CO_2 can be found in Appendix B, B.2.

Liquid Phase

To find a suitable liquid, literature is consulted for CO_2-liquid systems with no or low solubility. Systems with low or no solubility are typically not researched, as the goal of a supercritical extraction system is to dissolve a compound into the supercritical phase.

Looking at previous hydrodynamic studies, as discussed in Section 2.3.2, it can be seen that refined organic oils, such as olive, soybean, rapeseed, orange peel and fish oil, have been used with relative success. These systems are known to be partially soluble in supercritical CO_2 (92; 93; 94), making them non-ideal systems for hydrodynamic investigations.

The initial literature survey is narrowed to high molecular weight polymers or hydrophilic molecules, such as proteins or highly polar organic compounds, because of their low solubility in CO_2 due to its non-polarity. Further, the material has to be in the liquid phase or easily meltable.

Polymers were selected as an area of promise. To further narrow the scope it is noted that the solubility of amorphous polymers decreases with an increase in the surface tension of the polymer (95). This shows that, as the cohesive forces between polymer molecules increase, its solubility in the supercritical phase decreases and that the solubility is primarily governed by polymer-polymer interactions. This is in turn heavily dependent on the polymer structure and molecular weight. Thus high molecular weight polymers with high surface tension should yield the best results.

A study by Li, et al. (96) investigated hydroxyl and hydrogen-containing silicone oil in supercritical CO_2 and showed low solubility of the oil in the supercritical phase. Measuring cloud point pressures of silicone oil in Supercritical CO_2 they reported solubilities to be below 0.42 wt% at temperatures and pressures up to 55°C and 140 bar for an Mw 400 polymer. Thus silicone oils may be a good option, but a lack of further literature data makes it difficult to select a specific oil. A possible advantage to using silicone oil is that it is available in a wide range of molecular weights, providing a wide range of physical properties to test.

In addition to silicone oils, Li, et al. (96) also investigated polypropylene glycol (PPG), but found a higher solubility. Further they note that polyethylene glycol (PEG) should have a solubility lower than either that of silicone oil or PPG, warranting further investigation.

Drohmann and Beckman (97) studied the phase behaviour of polymers containing ether groups in CO_2, which included PEG, PPG and Polytetrahydrofuran or (PTHF). This study falls well within the supercritical pressure, but unfortunately fails to work above the supercritical temperature with experimental temperature given as 295.4 K. However, this study is still

significant as it provides a comparative basis for the different ether polymers. Of the fluids investigated, PTHF was the least soluble with an Mw 650 polymer only yielding a cloud point at pressures above 450 bar at more than 0.5 wt%. This marks PTHF as a strong candidate for future study. Unfortunately no further literature data was found concerning PTHF and an option with more literature data was preferred for initial runs. PEG was found to be more soluble than PTHF, but still a relatively good option, only becoming soluble at pressures above 200 bar. PPG performed the worst of the three, in concurrence with findings by Li, et al. (96).

PEG is more common in literature than PTHF, with several studies investigating its interaction with supercritical CO_2. A 400 Mw polymer was first investigated as a binary system in 1990 by Daneshvar, et al. (98) and later verified and expanded on to further PEGs by other sources (97; 99; 100; 101). PEG, like silicone oils, is available in a wide range of molecular weights leading to a wide range of possible physical properties.

The PEG covered most in literature is an Mw 400 polymer, also called PEG 400, with several sources of data available (97; 98; 99). PEG 400 is cheap and readily available, with acceptable solubilities and data available to correct for the solubility that does occur. A further advantage is that PEG 400 is highly soluble in water, which leads to easy cleaning of the system. Thus PEG 400 is selected as an acceptable first testing fluid.

Chemically pure PEG 400 was purchased from Merck Chemicals with a molecular weight distribution of 374-432 g/mol. The dynamic viscosity of the purchased PEG 400 was measured at atmospheric conditions using an Anton-Paar MCR501 rheometer. The values measured were found to compare well with literature (102) and can be seen in Appendix F. An MSDS sheet for PEG400 can be found in Appendix B, B.3.

4.3 Accuracy

As with any data gathered in research the accuracy is of paramount importance. Even with every precaution taken, certain factors can influence the accuracy of the measured data. These factors may include the following:

- Faulty calibrations. (See Appendix C for calibration procedures)
- Sensor drift.
- System hysteresis.
- System leakages.
- Experimental errors.

Every effort is made to eliminate and/or minimize these factors.

The accuracy of all sensors have been noted in Section 4.2.4, but is repeated below for the values directly relevant to the data acquired.

- All temperatures are measured with an accuracy of $\pm 1.5°C$ – a limitation imposed by the J type thermocouples available.
- Electronic pressure measurement is within an accuracy of ± 1 bar. Pressure gauges have an accuracy of ± 2.5 bar for 600 bar total and ± 1 bar for 100 bar total.
- The DP cell reports an accuracy of 0.075% of its range of 50 kPa, being 37.5 Pa.

The temperature probes are, where possible, installed with the tip in the middle of the flow channel to prevent wall effects and conduction from playing a role. Therefore, with proper calibration temperature accuracy should not be an issue.

For the pressure, even though measurement is reported with an accuracy of ± 1 bar, it is important to remember that an on/off control philosophy is followed. This causes momentary pulses in the system pressure, causing fluctuations in measurements. Further aggravating this phenomenon is the nature of the solvent and liquid feed pumps, which operate on the principle of positive displacement. This means that the feed to the columns occur in pulses, further increasing the system pressure instability. Using the logging system the pressure can be averaged over time, negating, to some extent, the effect of the pressure fluctuations.

4.4 Safety

As with any experimental setup it is important to identify hazards and eliminate them, or failing elimination, minimize the risks. To this end a preliminary hazard and operability study (HAZOP) was performed during initial design, followed by a full HAZOP after the system was finalized. The HAZOP is briefly discussed here, followed by short discussions of each of the main overall hazards and the way the risks were minimized in construction and operation.

4.4.1 HAZOP

The HAZOP study was performed using the guidelines and principles provided by Turton, et al. (55). All the process units, as seen in the PFDs in Figures 3-3 to 3-8, along with product pipelines, were considered in this study. Deviations in pressure, temperature, and flow were considered using the keywords, NO, LOW and HIGH. The full HAZOP documentation can be seen in Appendix E.

4.4.2 General Safety

As for any experiment, general personal protective equipment (PPE) is mandatory. This includes:

- A Lab coat.
- Closed shoes.
- Safety glasses.
- A hardhat.
- Ear plugs for extended periods of operation.
- Gloves when handling liquids.
- Insulated gloves and/or forceps when handling hot objects.

Under no circumstances can the plant be operated by someone working alone, due to the high pressure and temperature risks, as will be discussed in the following sections. It is also critical that the plant is not left unattended, due the possibility of a pressure build up.

4.4.3 High Pressure

High pressure is the main risk in the pilot plant setup. It is imperative that the operator of the plant remembers that high pressure implies that a large amount of potential energy is stored in the system; enough energy to cause serious injury or harm. This risk has been reduced during design, but can also be reduced by safe operation.

Safety During Design

When referring to pressure, the pilot plant is divided into two zones. Firstly, a lower pressure area focused around the separator and solvent preparation section with a maximum pressure of 80 bar and secondly, a higher pressure area that includes the liquid feed and column sections with a maximum pressure of 300 bar. This is a big difference in pressure and the zones were handled separately in design.

All the tubing and fittings for the lower pressure zone were purchased in stainless steel from Swagelok®. The Swagelok® components used are rated at 500 bar, allowing for a safety factor of approximately 6.3 for the low pressure section. Further, three pressure relief valves, set to 80 bar, have been installed in critical locations as identified in the HAZOP. The relief valves can be seen in the PFDs in Figures 3–3 to 3–6 in Section 4.2.

Tubing and fittings for the higher pressure zone were selected from Autoclave Engineers Inc. The 'medium pressure' product range was selected, rated at 1 380 bar. This calculates as a safety factor of approximately 4.6 for the higher pressure section. A single pressure relief valve,

set to 300 bar, has been installed in the high pressure section. Several burst disks, rated at 500 bar, have been installed next to local pressure gauges.

With regards to process equipment, some vessels from the old pilot plant, being the solvent buffer tank (V 2-1), the large column (C 3-2) and the Separator (V 4-1) fall under local high pressure equipment regulations, as specified in SANS 347. The vessels were pressure tested up to 125% and certified professionally by Raysonics Inspection, Test and Certification (RITC). The relevant documents can be seen in Appendix B, B.4. The small diameter column does not fall under regulation and was tested in-house to 125% using a dead weight tester.

The ratings for the individual components are summarised as follows:

- Small diameter column C 3-1 300 bar
- Large diameter column C3-2 324.24 bar
- All pumps (P1-1, P2-1, P 2-1) 300 bar
- Separator V 4-1 101.33 bar
- Solvent buffer tank V 2-1 74.32 bar
- Mass flow meter 100 bar

In both the pressure zones, redundant safety has been applied with regard to pressure. Not only has the system been designed and tested for pressures exceeding the working pressure, but the design and operating philosophies have been set up to ensure further safety.

Safety During Operation

It is important to ensure that the two pressure zones operate within their specifications. Pressure alarms have been implemented on the PLC which will turn off the pumps automatically if alarm setpoint pressures are exceeded, as discussed in Section 4.2.5. The alarms only cover the pressure around the column top product and the separator and not the whole system. It is vital that the system is monitored constantly through the various pressure gauges to avoid pressure build-up. The gas feed pressure should not rise significantly above the extraction pressure and the separator pressure should only be marginally above the gas bottle pressure.

In the case of a pressure build-up, the pumps should be switched off immediately. The excess pressure should be vented carefully and the reason for the pressure build-up should be identified. The troubleshooting guide in the plant manual identifies a few typical causes and how to resolve them.

4.4.4 High Temperature

Although operation at very high temperature is not planned for this study, the pilot plant is rated for a maximum temperature of 200°C. This is considered as a high temperature and precautions must be taken.

Safety During Design

As with pressure, two zones exist in the plant with different temperatures. The low temperature zone largely overlaps with the low pressure zone, with the same to be said for the high pressure and temperature zones.

The low temperature area encompasses the solvent preparation and recovery section (see Figure 4- 4) and temperature is governed by the refrigerator R1. This section can go as low as -10°C, but does not yield dangerous temperatures. The system is to be insulated to avoid losses and any risk from physical contact.

The majority of the remainder of the plant is heated by heaters H1 and H2. This section can go up to 200°C, which is enough to cause burns if it comes in direct contact with the skin. To limit this risk and to increase the heating efficiency the heating system will be insulated using mineral wool and fibre glass insulation. Heating pipes are further kept out of working areas as far as possible and heating valves are fitted with plastic handles to avoid burns when opening and closing valves.

Safety During Operation

During standard operation, direct contact with hot areas are not required, but if it becomes necessary the use of insulated gloves are recommended. Under no circumstances should hot oil connections be unscrewed during operation, as this can cause the hot oil to spray out. If a heating oil leak occurs during operation, stop the process and allow the system to cool down before attempting to repair the leak.

4.4.5 Flammability and Explosion

The hazard of flammable or explosive solvents are not directly relevant to this project, but has to be considered as a future possibility. Further, the plant is located next to a distillation column facility that often operates with flammable hydrocarbons, increasing the possible risk.

All of the major components in the plant are designed according to explosion-proof standards as received from the original pilot plant. Each individual piece of equipment is earthed to the pilot plant frame, which is in turn earthed to the electrical ground wire to avoid static build up

and electrical sparks. The sensors on the pilot plant can in future be explosion- proofed by adding safety barriers to the control box.

To further increase safety it is advised that the supercritical pilot plant and the adjoining distillation column facility is not operated at the same time.

4.5 Pilot Plant Operation

This section is concerned with the operation of the pilot plant and the methods used to acquire hydrodynamic data. A summary of the procedure followed is presented here, with a full, step-by-step experimental method available in Appendix F.

4.5.1 New Operators

Before the plant is operated, it is vital that the operator familiarizes him-/herself with the pilot plant and the relevant safety procedures, available in the pilot plant manual. After reading the plant documentation, available in the pilot plant manual, the operator should do a thorough check of the pilot plant and attend to any cleaning or maintenance required. The detailed procedure can be found in Appendix F, F.1.

4.5.2 Commissioning

In this study the pilot plant had to be commissioned for first time use. First all the electronic systems and sensors were calibrated following the calibration procedures as set out in Appendix C, C.1. The liquid feed pumps were also calibrated to provide calibration curve, in order to provide known liquid feed rates (Appendix C, C.2). All the alarms and automation sequences were then tested by triggering them manually. After testing all the safety interlocks it was deemed safe to start the commissioning of the overall plant. The testing of the alarms and automation sequences can be seen in Appendix C, C.3 and C.4.

The utility systems work independently from the pilot plant as a whole and were first commissioned individually. After this the system was cleaned and flushed to remove any residues left from the construction process. The pilot plant was then pressure tested up to operating pressures with demineralized water, after which it was dried thoroughly. A test run was then performed using only the supercritical phase. It was found the plant works as expected with no significant leaks or problems. The exact, detailed commissioning procedure is described in Appendix C, C.5.

4.5.3 Start-up Procedure

The following start-up procedure is followed. Figure 4- 2 is reproduced here to serve as a reference for the operating instructions.

Switch on the pilot plant, along with the cooling water, compressed air supply, heating units and refrigeration unit. In the case of operation with high temperatures it is advised that the heating units are turned on in advance. Load the liquid (or solid) feed of choice into the feed vessel V 1-1. Allow for enough time for the system to reach operating temperatures. Solvent is now loaded into the system from a cylinder. The fresh solvent is circulated over the cooling coils, E 2- 1 and E 2- 2, using the recycle loop and the 'Start-up' plc sequence. This speeds up the build-up of a liquid solvent level in the solvent buffer vessel, V 2-1.

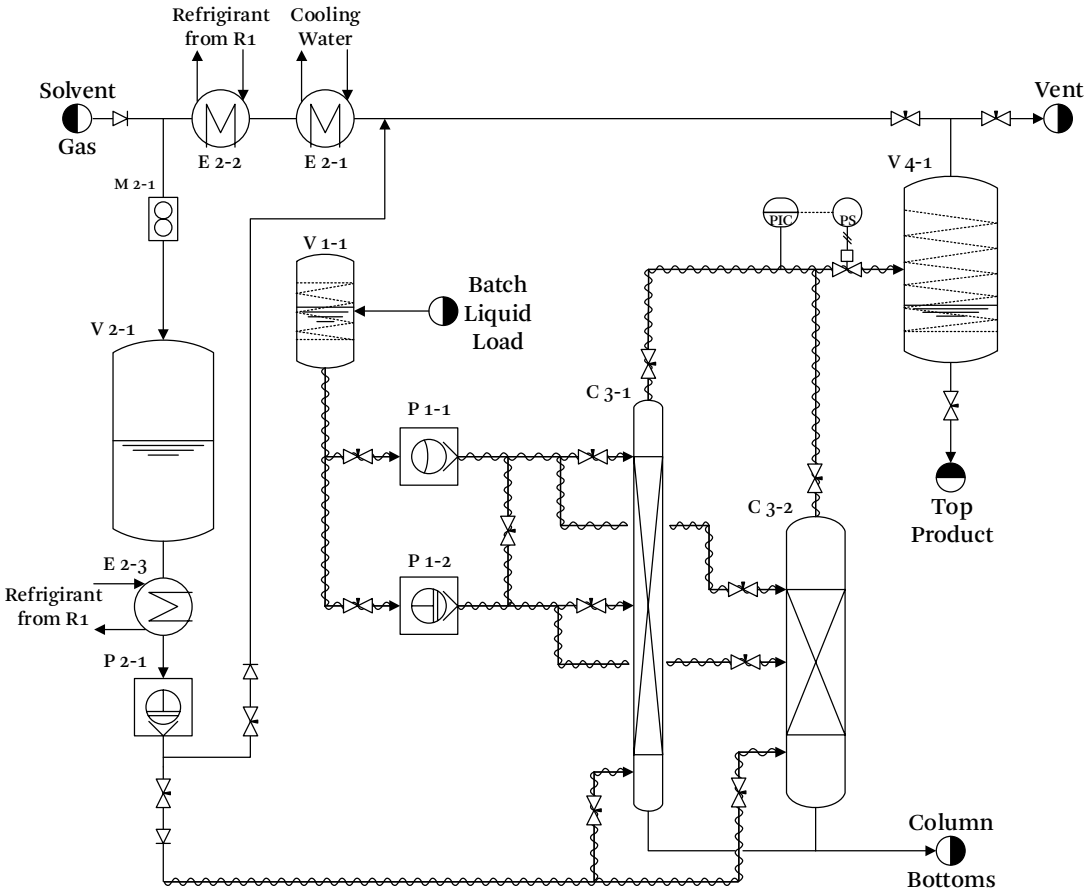


FIGURE LEGEND			
P 1-1	Feed Tank	M 2-1	Mass Dlow Meter
P 1-2	Small Capacity Diaphragm Pump	P 2-1	Solvent Feed Diaphragm Pump
V 1-1	Large Capacity Diaphragm Pump	V 2-1	Solvent Buffer Tank
E 2-1	Water Pre-cooler	C 3-1	Small Diameter Column
E 2-2	Chilled Condenser	C 3-2	Large Diameter Column
E 2-3	Pump Feed Chilled Pre-cooler	V 4-1	Overhead Product Separator

Figure 4- 2: Overview of the newly constructed pilot plant units.

Once a sufficient amount of liquid solvent has built up in the solvent buffer tank, monitored using the sight glass next to the tank, the solvent recycle loop is closed and the 'Start-up' sequence disabled. The pressure in the chosen column is then slowly increased to operating conditions by changing the setpoint of the pressure controller. Adjust the solvent feed rate until the desired rate is attained. Allow enough time for the system to reach equilibrium with the solvent feed alone. The pilot plant is now ready to start an extraction or hydrodynamic experiment.

4.5.4 Standard Extraction Operation

Check if the liquid feed is at the right temperature and that the chosen liquid feed pump is primed and ready. Select the appropriate liquid feed rate on the chosen pump and the appropriate column feed point by opening the necessary valves. The feed pump of choice can now be turned on to start the extraction experiment. Periodically decant the column bottoms and overhead product as required, weighing or measuring the volume obtained. The bottoms is monitored by the PLC using a level sensor to avoid build-up. Once the extraction run is completed, proceed to the shutdown procedure.

4.5.5 Hydrodynamic Measurements

In the place of standard extraction operations the pilot plant can be used to perform hydrodynamic experiments, in concurrence with the main aim of this project. Hydrodynamic measurements entail the measurement of the pressure drop over the column and liquid hold-up therein. The dry pressure drop and static liquid hold-up is measured for each new packing before any liquid is added. The wet pressure drop over and liquid hold-up in the column packing is measured at a range of defined liquid and solvent flow rates at equilibrium conditions.

Dry Pressure Drop

While the packing is unwetted the dry pressure drop can be measured. This is done by allowing the column to operate with only solvent flow. After reaching equilibrium, the pressure drop over the packing is noted, after which the solvent flow rate is changed and time again allowed for equilibrium to be achieved. This procedure is repeated to provide dry pressure drop data over a full range of solvent flow rates for a specific packing.

Static Liquid Hold-up

The static liquid hold-up is also measured using a dry column. The column is pressurised to operating conditions, after which the solvent feed is shut off. A known volume of liquid feed is

then pumped into the column using one of the liquid feed pumps. Time is allowed for the liquid to drain through the column packing, after which the liquid is collected and compared to the amount initially added. The difference is the static liquid hold-up, being the liquid that stays trapped in the column.

Wet Pressure Drop and Liquid Hold-up

After reaching equilibrium with solvent flow alone, the liquid feed is started. The column is allowed to reach a new equilibrium, while decanting the column bottoms as needed, as indicated by the level sensor. After equilibrium is reached the pressure drop over the column is noted. The column bottoms is then completely drained, after which all feed to the column is shut off. The liquid hold-up in the column is then allowed to collect in the bottom of the column, from where it is drained and weighed or the volume measured. The column is now operated with only solvent gas again. After equilibrium is achieved the procedure can be repeated for the next set of fluid flow rates. Once experiments are done the plant can be shut down using the shutdown procedure.

4.5.6 Shutdown

After operation the liquid feed to the column is shut off. After allowing for enough time for the column to drain the column bottoms and overheads is decanted. The column pressure is then slowly decreased to the extractor pressure by changing the pressure controller setpoint. The solvent feed pump can now be turned off. The operator can now choose to store the solvent in the system for future experimentation, or to drain the system of all solvent by opening and closing the necessary valves. Once the system is safe the oil heaters, refrigeration system, cooling water and pilot plant power can be turned off.

5. Experimental Results and Discussion

This section contains the experimental part of the project. First the parameters of the experimental system are established and confirmed. The pressure drop measurement is discussed and equilibrium conditions are defined. This is followed by the experimental results and discussion, with each hydrodynamic phenomenon individually, followed by a discussion of the combined results.

5.1 System Properties and Conditions

5.1.1 Column Properties

For experiments performed in this study only the large diameter column is used, as it is the only column currently fitted with a DP Cell. The column has an internal diameter, $Ø_I$, of 38 mm and packed height of 1.5 m. This compares well to the columns used in literature, as discussed in Section 2.3.2. It is further important to remember that the column is fitted with a permanent sintered metal demister. This demister will not significantly affect solvent flow or hydrodynamic readings, although it will deter entrained liquid drops from leaving the column.

The packing used is the ¼" Dixon rings, as discussed in Section 4.2.6. This is a relatively modern random packing and boasts small dead volumes and high surface areas for its relative size. A summary of relevant column and packing properties can be seen in Table 5- 1

Table 5- 1: Column and packing properties.

Description	Symbol	Value
Column Diameter	d / $Ø_I$	38 mm
Column Packed Height	H	1.5 m
Column Cross Sectional Area	-	1.134 x10^{-3} m^2
Column Packed Volume	-	1.701 x10^{-3} m^3
Particle Model Diameter	d_p	0.0006 m
Packing Void Fraction	$\in$	91 %
Packing Surface Area per Volume	a	900 m^2/m^3

5.1.2 Fluid Properties

Testing is to be performed at 313.15K (40°C) and 120 bar. This is, firstly, due to the supercritical hydrodynamic work by Stockfleth, et al. (13) and, secondly, because of the PEG 400/CO_2 binary system work by Gourgouillon, et al. (103), both being at 313.15K (40°C) and 120 bar. With the experimental temperature and pressure selected, the properties of the individual PEG 400 and CO_2 phases can be established.

As discussed in Section 4.2.6, CO_2 has a significant degree of solubility into PEG 400 under supercritical conditions (98). This solubility affects the properties of the PEG 400 liquid phase, in turn affecting the system hydrodynamics. Gourgouillon, et al. (103) measured the viscosity and density of PEG 400 saturated with CO_2 at various temperatures and pressures. This data is used to correct for the effect of CO_2 solubility in the experimental results.

At the selected temperature and pressure CO_2 causes the plasticization of the PEG leading to almost water like properties, as can be seen for viscosity in Figure 5- 1 and density in Figure 5- 2.

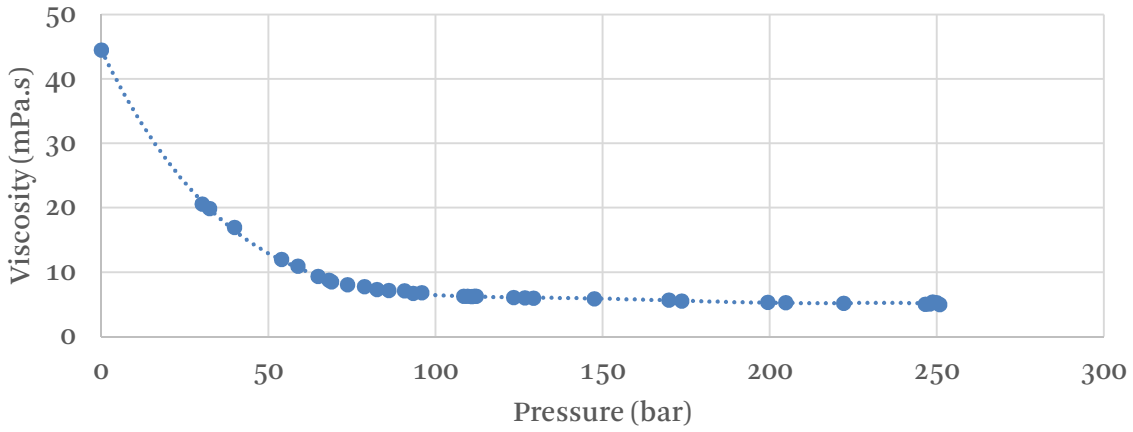


Figure 5- 1: Plot of CO_2-saturated PEG 400 dynamic viscosity vs CO_2 pressure at 313.25 K. (103)

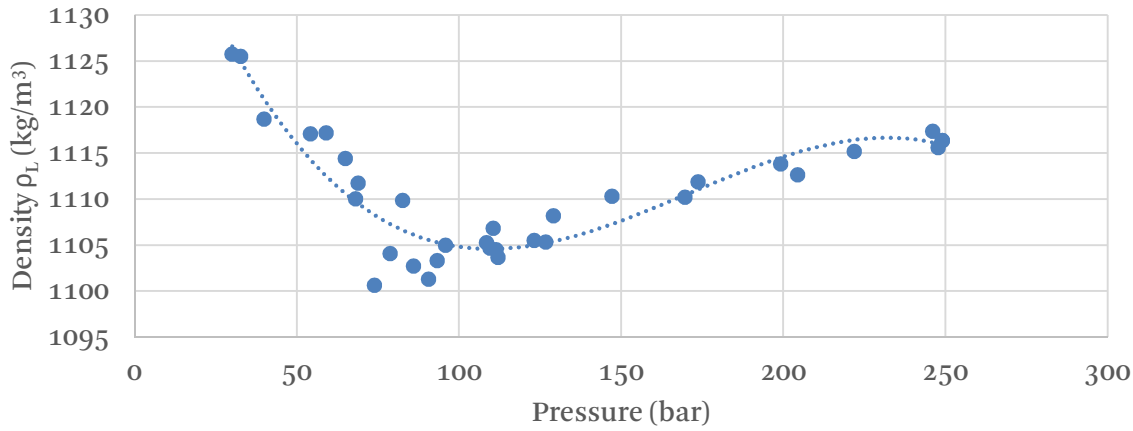


Figure 5- 2: Plot of CO_2-saturated PEG 400 density vs CO_2 pressure at 313.25 K. (103)

Pure component properties for the supercritical CO_2 phase are assumed to be the same as that of pure CO_2 under the same conditions. This assumption is justified by the extremely low solubility of the liquid in the supercritical phase, as discussed in Section 4.2.6. The properties for pure CO_2 are calculated using currently accepted correlations (18; 104).

The typical properties of both the supercritical and the liquid phases can be seen in Table 5- 2. The properties for CO_2 are calculated for each system, while the properties for PEG 400 is assumed to change little enough to be assumed constant.

Table 5- 2: Fluid properties at experimental conditions, 313.15K (40°C) and 120 bar.

Symbol	Description	Value	Source
ρ_L	PEG 400 density	1105 kg/m^3	Read from graph (103)
μ_L	PEG 400 viscosity	6.11e-3 Pa.s	Interpolated from (103)
ρ_G	CO_2 density	~717.76 kg/m^3	Calculated using (18)
μ_G	CO_2 viscosity	~5.85e- 5 Pa.s	Calculated using (104)

5.1.3 DP Cell Readings and Calibration offset

For ease of calibration, and to ensure a repeatable reference point, the DP Cell is zeroed at atmospheric conditions with the column open to air. The column is then pressurised and heated to the operating conditions of 313.15K (40°C) and 120 bar. If the DP cell is operating correctly, the pressure drop reading over a static system should be equal to, or at least very close to, zero. It was found that the DP cell did not stabilize at zero, but at a negative pressure of ~-2400 Pa, as can be seen in Figure 5- 3.

This is problematic, as an unknown factor was influencing the DP cell reading. After several tests it was found that this was a constant error.

In Section 4.2.4 it was stated that the DP cell is connected to the column by means of capillaries to enable the DP cell to operate at high temperatures. These capillaries dissipate heat and allow the DP cell to operate at manageable temperatures. It is thought that these capillaries, operating at ambient temperatures, are well below the critical temperature of CO_2 (304.25K or 31.1°C), leading to a more dense fluid, possibly even liquid, CO_2 layer forming. This dense fluid layer will build up in the capillaries to a stable level and lead to the pressure imbalance. The capillaries are of sufficient length to cause such problems, as can be seen in Figure 5- 4.

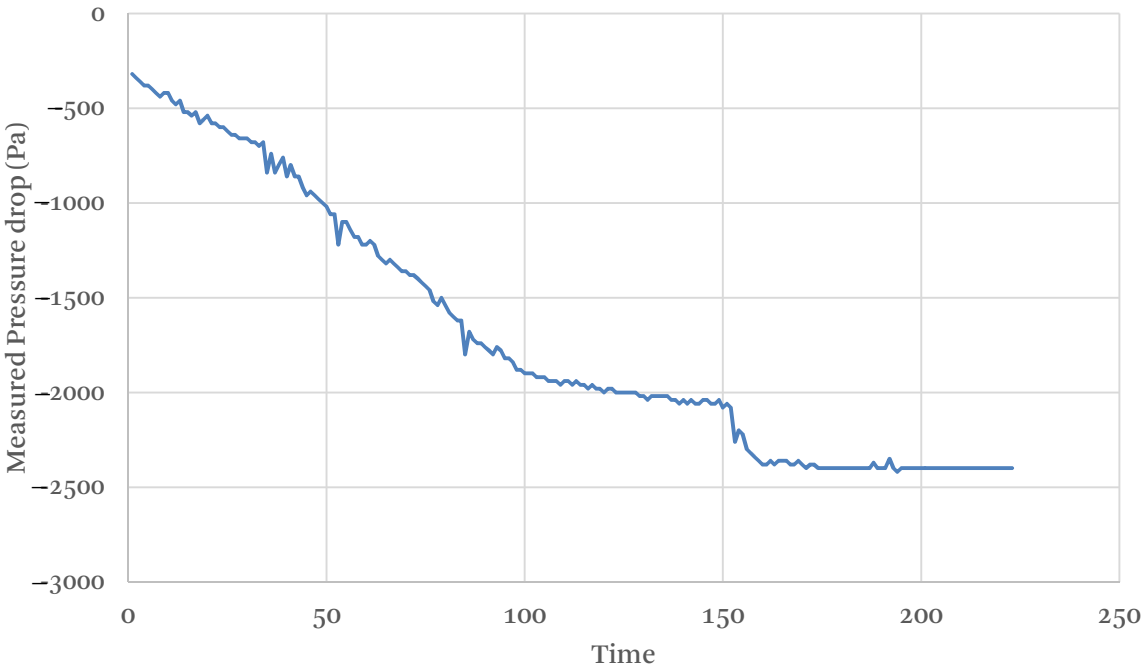


Figure 5- 3: DP Cell pressure drop reading for a static system at 313.15K (40°C) and 120 bar.

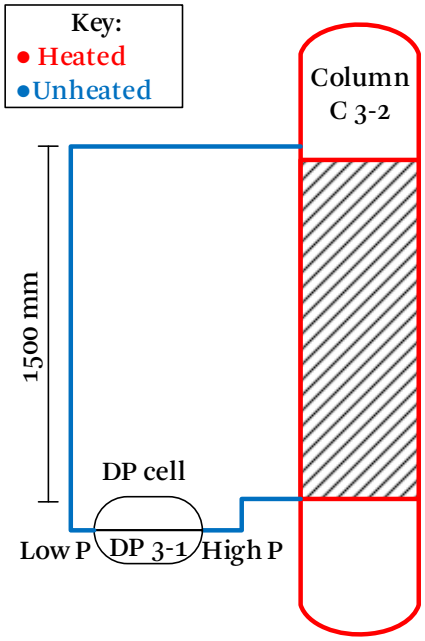


Figure 5- 4: Schematic representation of the DP cell, column and capillaries.

To test this hypothesis, a twofold approach was followed. First, the pressure difference that can be caused by the capillaries filled with dense fluid, was calculated. This is done by using the ambient laboratory temperature of 293.15K or 20°C to calculate a CO_2 density of 878.10 kg/m^3 at 120 bar (18). Subtracting the column supercritical density of 717.76 kg/m^3, as defined in Section 5.1.2, the net difference is acquired.

The difference between the phase densities, along with the height difference, causes a hydrostatic pressure difference that can be calculated as follows:

$$\Delta P = \Delta\rho \times g \times h$$
$$= (878.10 - 717.76) \times 9.81 \times 1.5$$
$$= 2360 \text{ Pa}$$

This correlates very well with the measured pressure drop op 2400 Pa, making a denser CO_2 phase settling in the capillaries the likely culprit.

To confirm this we come to the second part of the hypothesis testing. The low pressure side capillary, being of longer length and higher total elevation, is the likely cause of the imbalance. The system is brought to the same equilibrium point with a negative pressure drop of $\pm$2400 Pa. The low pressure side capillary was then heated using a hot air gun. The applied heat should force the CO_2 dense fluid in the tube back into the less dense the supercritical phase, cancelling out the pressure difference.

After applying heat the pressure drop reading immediately started to rise and, with continued heating, stabilized at ~10 Pa. This test confirmed that high density CO_2 is present in the capillaries and is the source of the inaccuracy. Indeed in his doctoral dissertation Stockfleth (76) mentions similar problems of temperature differences in capillaries.

Stockfleth (76) addressed the problem of the sensor capillaries affecting readings, by trying to eliminate the effect of hydrostatic pressure during an experimental run. When measuring the pressure drop of a system with both phases in equilibrium, Stockfleth (76) states, correctly, that the differential pressure sensor measures both the pressure drop caused by flow, and that caused by the hydrostatic differences. In order to mitigate the effects of the hydrostatic pressure drop, he theorizes that any change in hydrostatic pressure will happen at a very slow pace, and any change in differential pressure will occur rapidly. To measure the pressure drop, Stockfleth (76) allows the system to reach equilibrium and notes the reading of the differential pressure sensor. The feed to the column is shut off, and the reading on the differential pressure sensor is noted again. The difference between the two readings is then presented as the pressure drop caused by flow. No further explanation or justification of the assumption is made by Stockfleth (76).

At first it seems to be a reasonable assumption to assume the pressure difference caused by the phase flow will equalise quickly, but it is questionable how fast exactly, and if the resulting reading will provide an accurate representation. The equalization of the pressure in the column will happen in the form of a pressure wave. In wave theory, the propagation of pressure waves, a type longitudinal wave, happen at the speed of sound in the medium. In the classical phases

of matter the speed is dependent on the density of the medium, with higher densities causing faster wave propagation. Supercritical fluids have, however, been proven to provide significant resistance to the propagation of waves, in spite of the phase's elevated density, leading to speeds several times lower than that of sound in air (105). Further the packing and the liquid in the column actively hamper the propagation of the pressure wave, and may even resonate with the wave, causing further disruptions. It is therefore not evident that the pressure will equalize fast enough, or indeed equalize at all before equilibrium is significantly disturbed.

In contrast with the method used by Stockfleth (76), this project assumes the effect of the hydrostatic pressure to be constant, meaning a correction factor can be applied to gathered data to provide an accurate reading. This is a reasonable assumption if the conditions in the system, especially the capillaries stay the same. As soon as a stable dense phase layer is formed in the capillaries the pressure sensor should provide consistent, predictable readings. The DP cell offset is tested before experimentation every day and was found to stay within 5% of the value of 2360 Pa. To investigate the possibility of the lab temperature changing significantly during the day and affecting the hydrostatic pressure drop, runs were performed during the day on occasion, with similar results. Thus the value of 2360 Pa is assumed as a constant offset and applied to all pressure drop readings.

To ensure the hydrostatic pressure is constant over all readings, the system is operated with only CO_2 before each experimental run, as discussed in Section 4.5. Enough time is allowed to reach equilibrium before each run, allowing a stable layer of CO_2 to form in the capillaries. This level should be the same as the level formed under static conditions, as the capillaries measure shear pressure drop mass transfer in and out of the capillary is not significantly influenced by flow.

The starting pressure drop of all the runs at a specific solvent flow rate are compared and an experiment is not started until the sensor stabilizes at the same pressure as for previous runs. For a new solvent flow rate equilibrium is achieved at a known rate, after which the solvent flow rate is then changed to a new rate, yielding a trustworthy starting pressure drop. It is found the system stabilizes at or very close to the dry pressure drop value for any given solvent flow rate.

Ideally the effect of the hydrostatic pressure should be eliminated completely by using fluid filled capillaries with a diaphragm system installed at the column. Unfortunately the time constraints of this project did not allow for this undertaking.

5.1.4 Equilibrium Condition

Equilibrium in the column was assumed on the basis of a stable pressure drop. During an experimental run the column is first operated with only supercritical CO_2 at the desired gas flow rate. Time was allowed until the pressure drop over the column stabilized. For all runs at the same solvent flow rate the value of the pressure drop was found to be the same with the column only operating with the supercritical fluid, as discussed in Section 5.1.3. This confirms that the hydrostatic level in the capillaries has built up sufficiently. The liquid feed pump is then turned on at a chosen liquid rate and time is again allowed for the system to stabilize or flood.

An example of the change of the pressure drop during an experimental run can be seen below in Figure 5- 5. In the figure the zero time value denotes the point where the liquid feed was turned on.

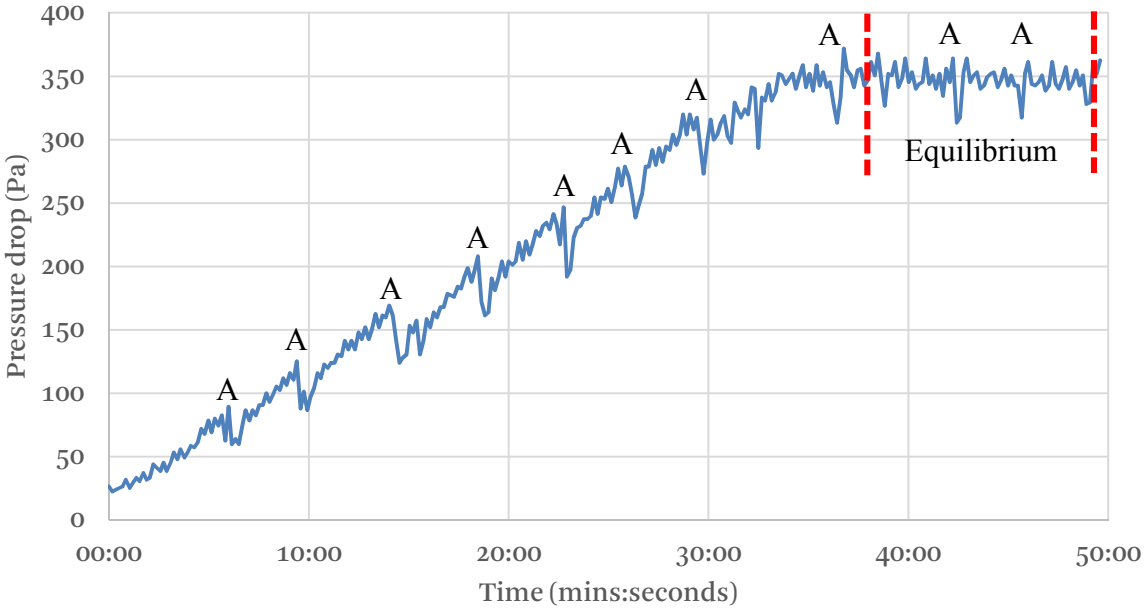


Figure 5- 5: Example of experimental run pressure drop data.
Supercritical phase flow rate 0.474 kg/min, liquid flow rate 0.093.kg.min

In this system a regular interruption in the trend can be observed, also visible in the equilibrium part of the graph. This phenomenon was linked to the decanting of the column bottoms. Decanting is indicated on the graph by the points labelled ' A ' in the figure.

Even though the decanting of the bottoms was done as slowly and carefully as possible, it still affected the equilibrium in the column, as can be seen in Figure 5- 5. This was taken into consideration during experimentation and data gathering, and sufficient time was allowed for the system to recover from the disturbance caused by decanting, before averaging logged data to determine the experimental results.

5.2 Experimental Results

Due to the nature of the pilot plant it is easier to assume a constant supercritical phase flow rate for a system and vary the liquid feed rate. Five supercritical phase flow rates were investigated over several liquid flow rates. General observations are made and the results are discussed with respect to the measured dry pressure drop, liquid hold-up, wet pressure drop, flooding, and entrainment phenomena, comparing results with literature where possible.

In this section the terms 'supercritical phase' and 'gas' or 'gaseous' are used interchangeably. This is to accommodate the models and correlations, many of them referring to a gas state with respect to subcritical hydrodynamics. In the case of a supercritical column the 'gas' state implies the supercritical phase flowing through the column, or in other words the less dense state flowing through the column.

5.2.1 Summary of Experimental Results

A summary of the experimental results can be seen in Table 5- 3.

The column top liquid alarm mentioned in Table 5- 3 refers to LE 3- 2, being an optical level sensor 15 mm above the top of the packing. This liquid level is used to investigate if a liquid level on top of the packing is present. This liquid level is not presumed to imply flooding, but rather the 'flooding' condition is determined by the column overheads, as will be discussed in Section 5.2.6.

Mass flow rates were checked using a mass balance over the system. Some discrepancy between the mass flow into the column and the mass flow measured was found, but can be ascribed to system instability, dissolved CO_2 in the liquid, and differing PEG densities due to temperature and pressure. Correcting for these factors provided a reconciled mass balance, which is used in calculations.

All calculated values used in the remainder of this section can be viewed in Appendix F. Raw experimental graphs can also be seen in Appendix F for all experimental runs.

Table 5- 3: Summary of experimental results.

Gas Flow Rate (kg/min)	Gas Density (kg/m^3)	Gas Viscosity (Pa.s)	Liquid Mass Flow Rate (kg/min)	Solvent /Liquid Feed Ratio	Average Column Temp (°C)	Average Column Pressure (bar)	Run Duration (mins)	Measured Column Bottoms (g/min)	Measured Column Tops (g/min)	Measured Liquid Holdup (g)	Column Top Liquid Alarm	Flooding	Dry Pressure Drop (Pa/m)	Pressure Drop per unit length (Pa/m)
0.453	716.02	5.829E-05	0.038	12.08	40.00	119.4	24.83	27.75	1.78	115.42	N	N		361.3
0.488	716.06	5.843E-05	0.056	8.69	39.99	119.7	45.98	28.58	0.95	222.83	N	N		464.0
0.462	728.54	5.997E-05	0.075	6.19	38.88	119.6	36.12	53.80	1.36	410.19	N	N	212.7	921.3
0.474	728.23	5.992E-05	0.093	5.07	38.91	119.6	49.83	38.57	12.33	1260.11	Y	Y		3468.7
0.442	712.72	5.786E-05	0.112	3.95	40.24	119.2	33.83	55.13	12.19	1065.18	Y	Y		3491.3
0.562	709.13	5.740E-05	0.038	14.97	40.43	118.7	42.42	26.52	1.55	154.86	N	N		468.7
0.564	704.6	5.682E-05	0.056	10.05	40.80	118.6	31.20	40.99	1.40	284.77	N	N		1001.3
0.593	713.96	5.803E-05	0.075	7.93	40.16	119.3	43.00	31.45	1.62	651.36	N	N	299.3	1632.4
0.578	718.2	5.858E-05	0.093	6.19	39.88	119.7	29.33	29.13	19.31	1193.77	Y	Y		3394.0
0.562	712.81	5.788E-05	0.112	5.02	40.40	119.8	23.83	22.95	22.32	1218.89	Y	Y		3539.3
0.642	722.61	5.917E-05	0.038	17.10	39.60	120.2	29.00	22.09	2.06	173.68	N	N		654.0
0.670	725.83	5.961E-05	0.056	11.93	39.58	121.3	22.17	26.50	1.73	279.1	N	N		1423.3
0.672	721.3	5.901E-05	0.065	10.27	39.96	121.1	52.83	38.67	1.72	630.41	N	N		3057.3
0.667	724.45	5.942E-05	0.075	8.92	39.40	120.1	40.67	45.35	2.44	670.16	Y	N	450.7	3279.3
0.670	726.38	5.968E-05	0.084	7.97	39.19	120.0	26.50	26.52	9.76	1110.69	Y	Y		3076.0
0.656	721.23	5.899E-05	0.093	7.03	39.73	120.2	28.05	26.13	15.54	1129.93	Y	Y		3170.0
0.656	733.06	6.060E-05	0.112	5.86	38.95	121.6	20.17	23.83	19.77	1101.91	Y	Y		3299.3
0.768	706.01	5.700E-05	0.038	20.46	40.87	119.3	39.33	12.57	2.03	168.12	N	N		1082.7
0.778	733.19	6.059E-05	0.056	13.86	38.10	118.3	34.75	17.51	3.02	284.27	N	N		1116.0
0.760	705.36	5.692E-05	0.075	10.17	40.90	119.2	37.45	33.95	2.77	750.54	Y	N	546.0	2340.7
0.760	708.59	5.733E-05	0.093	8.14	40.45	118.6	37.17	20.65	19.23	1074.10	Y	Y		3111.3
0.796	706.6	5.707E-05	0.112	7.11	40.68	118.8	39.83	21.99	35.67	1052.86	Y	Y		3214.7
0.860	726.08	5.964E-05	0.038	22.9	39.40	120.7	50.88	16.75	2.43	158.1	N	N		1412.7
0.858	697.58	5.595E-05	0.056	15.3	41.80	120.0	43.83	30.26	1.97	291.3	N	N		1192.7
0.855	713.28	5.795E-05	0.075	11.4	40.60	120.7	68.43	39.49	2.43	953.4	Y	N	799.3	3339.3
0.899	738.31	6.132E-05	0.093	9.6	38.10	120.3	31.53	21.55	20.04	1083.2	Y	Y		3492.7
0.870	707.79	5.725E-05	0.112	7.8	41.40	121.8	28.47	19.57	23.83	1013.5	Y	Y		3246.0

5.2.2 General Observations

During the experiments several general observations of interest were made:

- Depending on the supercritical phase flow rate, the first column bottoms were observed between 4 and 9 minutes into the run. At higher supercritical phase flow rates the initial liquid took the most time to pass through the column, indicating that the resulting higher shear forces detains the liquid in the column for longer.
- Pressure fluctuations in the system tended to be a bigger issue at low supercritical phase flow rates. This is due to the pressure control philosophy and the overhead choking done with NV 4-1, as it is more difficult to choke the overheads at a lower flow rate.
- In systems with flooding the system initially yielded normal rates of column bottoms. As the column reached a point where it starts to flood the bottoms production rate drastically decreased. The same type of phenomenon was observed in the column overheads, with the rate of overheads increasing drastically after reaching the flooding point. As both the column bottoms and overheads were decanted manually at intermediate intervals, this observation is not substantiated by data and confirmation is required.

5.2.3 Dry Pressure Drop

Before any experiments were performed using liquids, the dry pressure drop of the packing was determined at operating conditions. The measured pressure drops, as can be seen in Table 5- 3, showed a direct correlation with the gaseous phase superficial velocity u_G, and hence the gas capacity factor F_G. The pressure drop is plotted against the gas capacity factor and can be seen in Figure 5- 6.

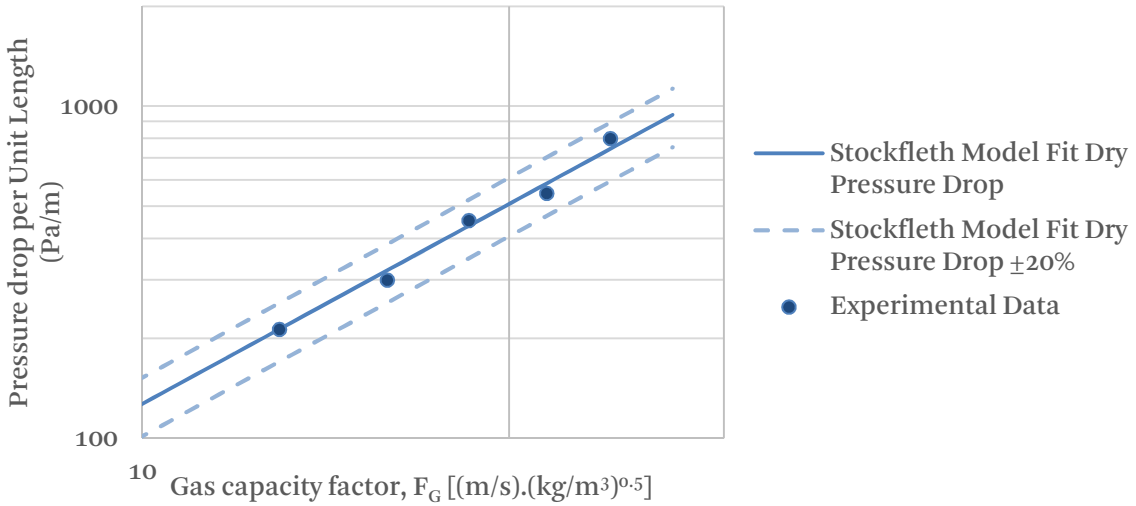


Figure 5- 6: Experimental dry pressure drop and model fit vs. gas capacity factor.

No experimental literature data is available for easy comparison, but the data can be compared to the model for Raschig rings and Berl saddles by Stockfleth, et al. (13), described in Section 2.4.1, Equation [9]:

$$\frac{\Delta P_0}{H} = \frac{3\psi\rho_G u_G^2(1-\epsilon)}{4d_p\,\epsilon^{4.65}} \text{ with } \psi = \frac{K_1}{\mathrm{Re}_G} + K_2 \text{ where } K_1 = 23 \text{ and } K_2 = 1.2 \qquad [9]$$

Comparing the predicted pressure drops with the measured pressure drops in Table 5- 4, it can be seen that they differ greatly.

Table 5- 4: Comparison of measured and calculated dry pressure drop values using parameters as proposed by Stockfleth, et al. (13)

Superficial Gas Velocity u_G x 10^3	ΔP_0 Calculated (Pa/m)	ΔP_0 Measured (Pa/m)
9.51	17.3	212.7
11.67	25.0	299.3
13.61	33.2	452.7
15.77	43.5	546.0
17.78	54.5	799.3

Some degree of difference in pressure drop can be ascribed to differences in packing and system operation, but not differences of this size. The differences between experimental systems will be discussed in more detail in Section 5.2.8. The remainder of the difference can be explained by differences in measuring method, as discussed in Section 5.1.3.

Investigating the differences between the predicted and measured pressure drop values Table 5- 4, it can be seen that they differ by a constant multiple from the calculated results. This implies that the model can be adjusted to fit the experimental data. Using Excel solver to minimise the difference between the model and the calculated values, new values for K_1 and K_2 are determined as $K_1 = 0$ and $K_2 = 18.8$. The value of $K_1 = 0$ may seem unacceptable at first, but manual varying of this value showed the term had a negligible influence on the model fit of the experimental data. Hence the term K_1, and the gaseous Reynolds number Re_G, can effectively be neglected in the calculation for the friction factor, leading to the friction factor being proposed as $\psi = 18.8$. This is only proven for the range of the Reynolds number that has been tested, being $70 < \mathrm{Re}_G < 130$, which in well into the laminar flow regime for gaseous flow, with the typical crossover at a Reynolds number of 2000. (See Appendix F, F.2 for calculated values). A very good fit of the experimental data is found when plotting the model with the new friction factor in Figure 5- 6.

5.2.4 Liquid Hold-up

As discussed in Section 2.2.6, the liquid hold-up consists of a static and a dynamic part. These parts will be investigated separately.

Static Liquid Hold-up

An attempt was made to measure the static liquid hold-up at operating conditions using the method described in Appendix F, 4.1 After allowing enough time for the system to drain the liquid was decanted and weighed. It was found that virtually no liquid is retained in the column if enough settling time is allowed. This agrees with literature, as discussed in Section 2.4.2.

A further proof of negligible static hold-up is seen in comparing the pressure drop over a wetted column to the dry pressure drop. These values correlated closely, as discussed in Section, 5.1.3.

Dynamic Liquid Hold-up

The dynamic liquid hold-up is also measured for each run and can be seen in Figure 5- 7, plotted against the liquid superficial velocity, u_L .

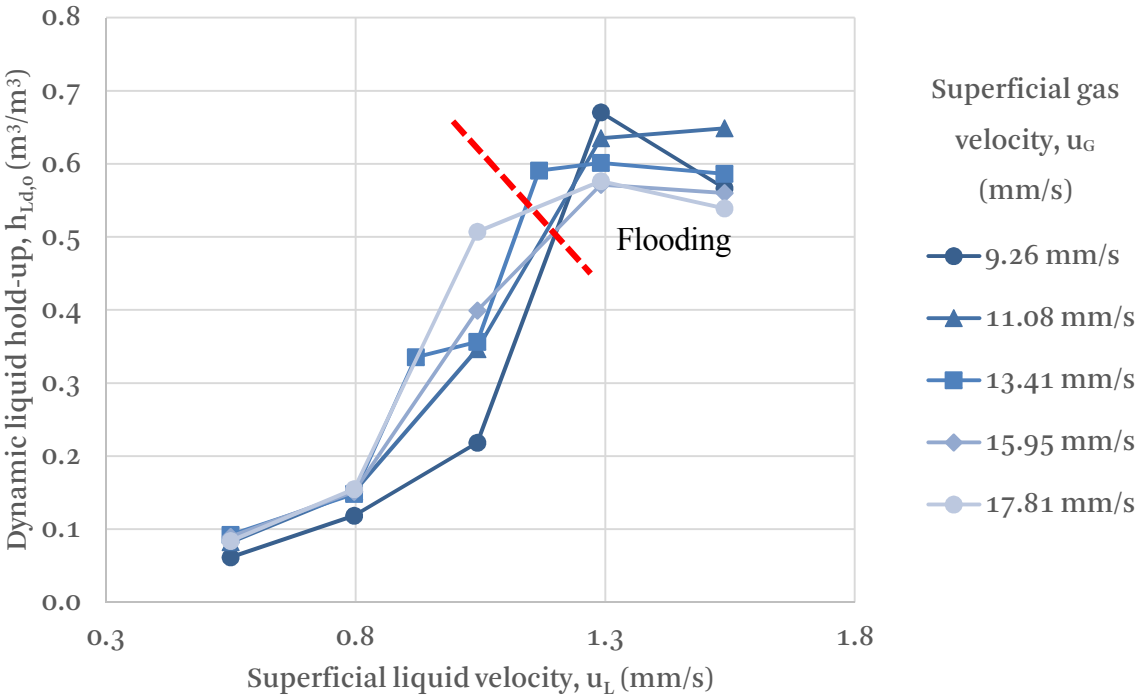


Figure 5- 7: Dynamic liquid hold-up vs. superficial liquid velocity.

The liquid hold-up is seen to increase with increasing superficial liquid velocity. The trends follow on each other with a lower superficial gas velocity generally yielding lower liquid hold-ups. The trends smoothly increase until the flooding phenomenon is reached, except for a single point in the 13.41 mm/s superficial gas flow rate appearing higher than expected,

possibly indicating an experimental error. An estimated flooding region is indicated on the graph as determined using the column overheads. Flooding will be discussed in Section 5.2.6.

The individual liquid hold-up trends show a rapid increase similar to that of subcritical phenomena, but instead of increasing indefinitely, seems to reach a type of universal maxima. This maximum value is exhibited when the column floods and can be explained by the liquid forming a liquid layer on the top of the packing. This liquid layer is then simply pushed into the column overheads and the majority of the liquid short- circuits. This is confirmed when looking at the rate of column overheads, which exhibit a drastic increase in overheads noted at these 'flooding' values.

To graphically represent the interplay between the hold-up and overheads the respective values are plot together in Figure 5- 8 for comparison.

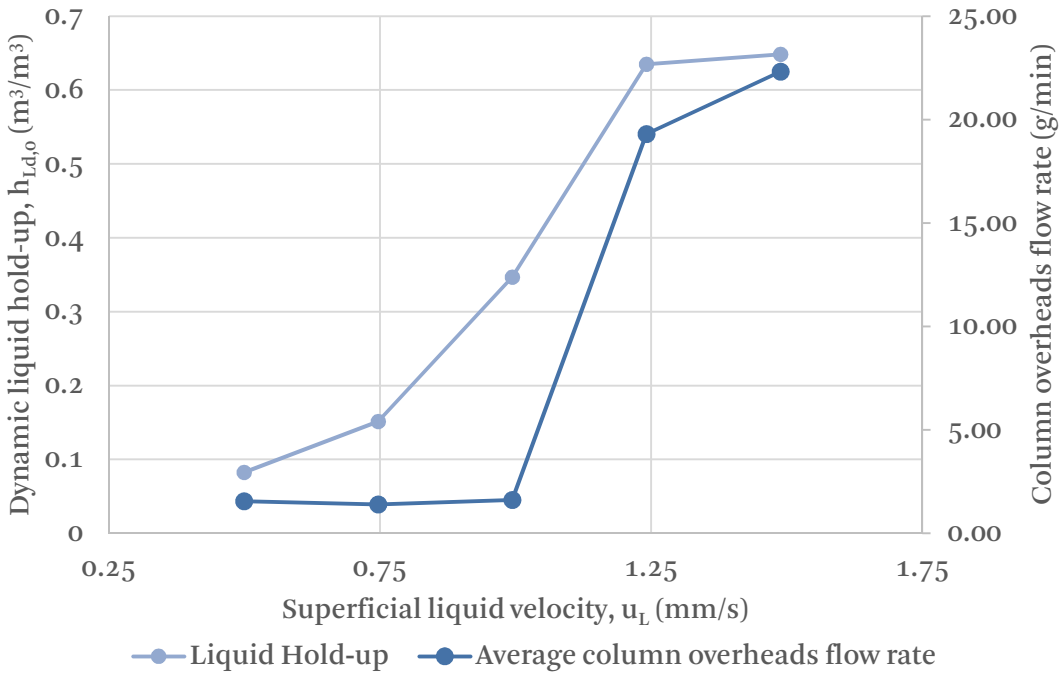


Figure 5- 8: Dynamic liquid hold-up and average column overheads vs. superficial liquid velocity for a superficial gas velocity of 11.08 mm/s.

Literature data by Stockfleth, et al. (13), is available at the same operating conditions for a water/Raschig ring system and is plotted alongside experimental results for comparison. This can be seen in Figure 5- 9.

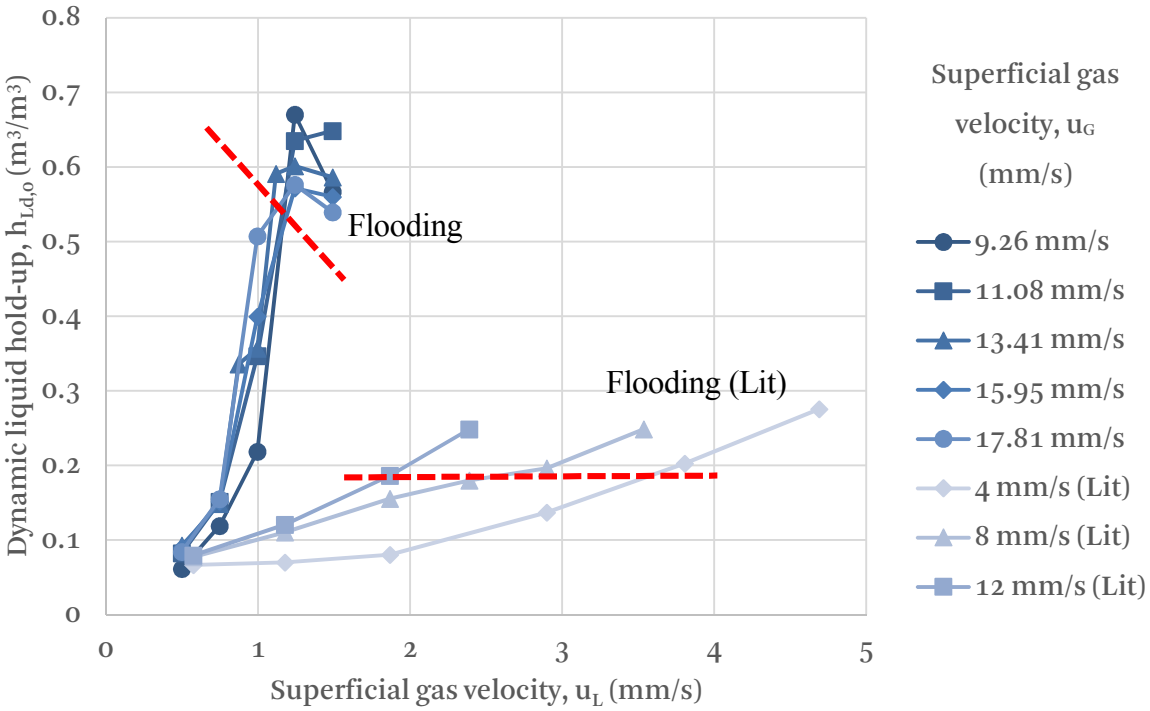


Figure 5- 9: Dynamic liquid hold-up vs. superficial liquid velocity.
Includes literature values for water and Raschig rings at the same operating conditions. (76)

Comparing the experimental liquid hold-up with literature values it can be seen that the values are of similar magnitude. However, the literature values show similar flooding values only at much higher superficial liquid velocities. Flooding was observed at much lower liquid rates than in the literature data. This can be attributed to several differences between the experimental and literature datasets.

Firstly, it is important to note that the Raschig rings used by Stockfleth are much smaller in diameter at 5 x 0.5 mm, versus the 6.35 x 6.35 mm Dixon rings used in this study. This translates to the surface area of the literature packing being 3.7 times larger than that of the Dixon rings used. The increased surface area should, however, lead to a higher liquid hold-up, and not a smaller liquid hold-up. Secondly, the packing geometry and type also differs significantly, with the literature using solid raschig rings, versus the stainless mesh Dixon rings used during experimentation. The Dixon ring geometry should naturally increase liquid hold-up, and when combined with the mesh construction, should account for the majority of the difference between literature and measured data. Thirdly, it has been shown that both liquid and vapour properties influence column hydrodynamics (106). The difference in operating fluids can also

account for the differences in measured hold-up. Finally the column used in literature has a diameter of 25 mm, slightly smaller than the 38 mm column used in this study. The effect of column diameter on hydrodynamics is unknown for supercritical conditions and small diameter columns.

The experimental data points at the first two superficial liquid flow rates are thought to be below the loading point. As with the dry pressure drop, the model proposed in Section 2.4.3 fails to predict the liquid hold-up by significantly under predicting values. Attempting to regress new empirical parameters for the data proved futile, with the model unable to predict liquid hold-up. This implies the initial assumption of the data points for both superficial liquid flow rates being below the loading point, to be incorrect. Regressing new parameters for data at only one superficial liquid velocity will not provide an accurate model and is not advisable.

The model for liquid hold-up beyond the loading point is dependent on the model of the hold-up below the loading line. As the model below the loading point cannot be verified, no sensible model fit for the liquid beyond the loading point can be performed.

5.2.5 Wet Pressure Drop

The wet pressure drop is measured for each run and can be seen in Figure 5- 10 plotted against the liquid superficial velocity, u_G .

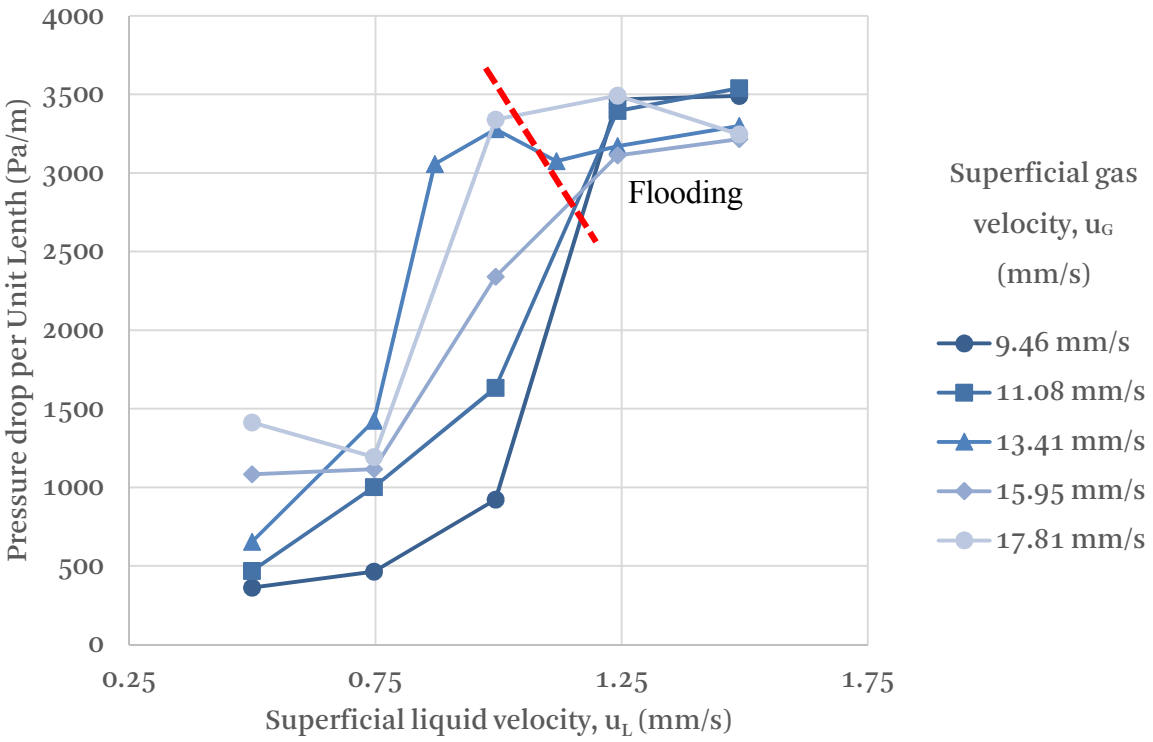


Figure 5- 10: Wet pressure drop per unit length vs. superficial gas velocity.

Similarly to the liquid hold-up, the wet pressure drop increases with increasing superficial liquid velocity up to the flooding point. The pressure drop is also seen to increase with increasing superficial gas velocity in the same region, except for two data points at very low superficial liquid velocity. An estimated flooding region is indicated on the graph as determined using the column overheads. Flooding will be discussed in Section 5.2.6.

The individual pressure drop curves can be seen to increase slowly at first and then rapidly to a common maximum, again similar to the liquid hold-up. This can then also be ascribed to a liquid layer forming at the top of the column and the liquid short circuiting. It is thought that the pressure caused by the supercritical phase added at the bottom of the column builds up to a level where it cancels out the hydrostatic pressure of the liquid, taking the buoyancy caused by the supercritical phase into account. Indeed flooding takes much longer at low superficial gas velocities, indicating a gradual pressure build up.

Literature data by Stockfleth, et al. (13), at the same system pressure and temperature for a system with water over Raschig rings is available for comparison. A comparison of experimental data and literature data can be seen in Figure 5- 11.

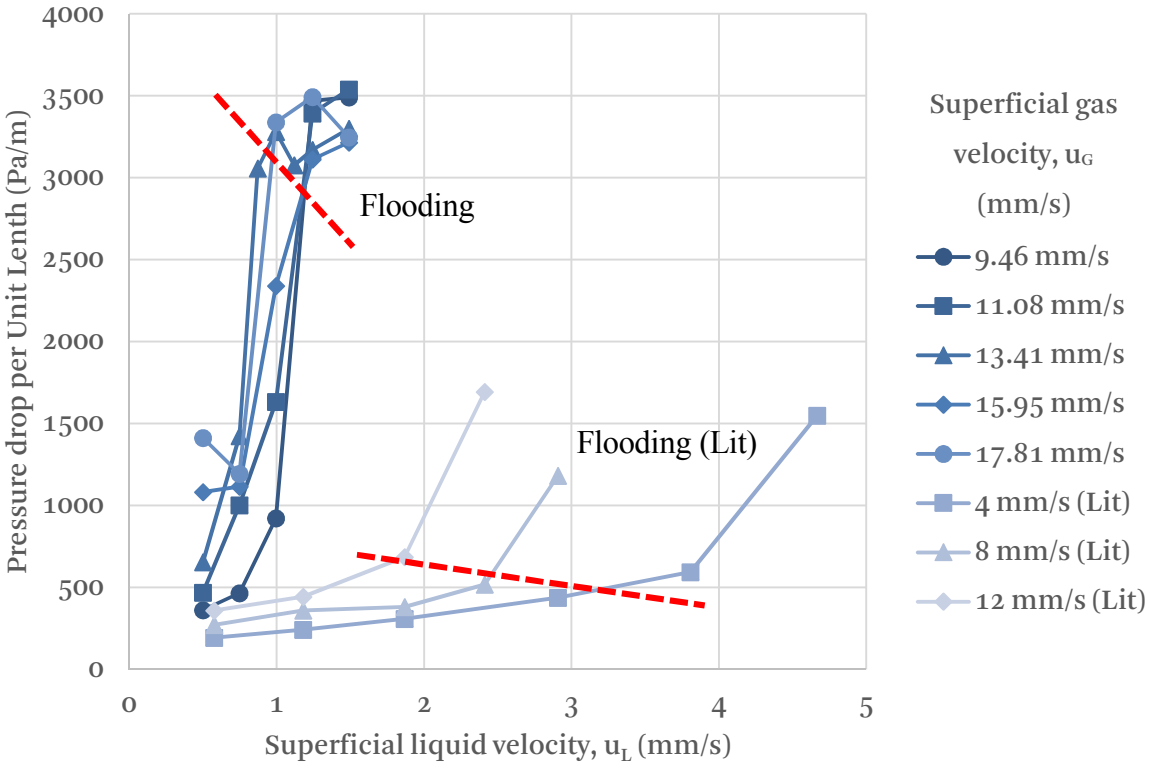


Figure 5- 11: Dynamic liquid hold-up vs. superficial liquid velocity.
Includes literature values for water and Raschig rings at the same operating conditions. (76)

When comparing the experimental and literature pressure drop a similar situation to the liquid hold-up behaviour is observed. The literature pressure drop curve is positioned at higher superficial liquid velocities and again the literature values as a whole are smaller than the experimental values observed.

It is expected that the higher the liquid hold-up, the higher the resulting pressure drop that occurs. The liquid hold-up and pressure drop is therefore interdependent and changes to the one will effect changes in the other. The differences between the measured and literature pressure drop has already been explained in light of the differing column packings, diameter and the liquids used. The mutual dependence of liquid hold-up and pressure drop implies that the same reasoning used to explain the differences between experimental and literature liquid hold-up, applies to the pressure drop, explaining the difference between measured and literature values in Figure 5- 11.

It can also be reasoned that the difference between literature and experimental pressure drop trends can be explained by the difference in measurement technique, as discussed in Section 5.1.3. This can be investigated by keeping the interdependence of liquid hold-up and pressure drop in mind. If the measurement technique affected the pressure drop reading, a different trend will be observed when plotting the pressure drop vs. the liquid hold-up. This comparison will also, to some extent, eliminate the differences caused by the packing or liquid properties, as the response of a system should show the same typical trend. A plot of the pressure drop vs. the liquid hold-up is made for both experimental and literature data for values below the flooding region, as can be seen in Figure 5- 12.

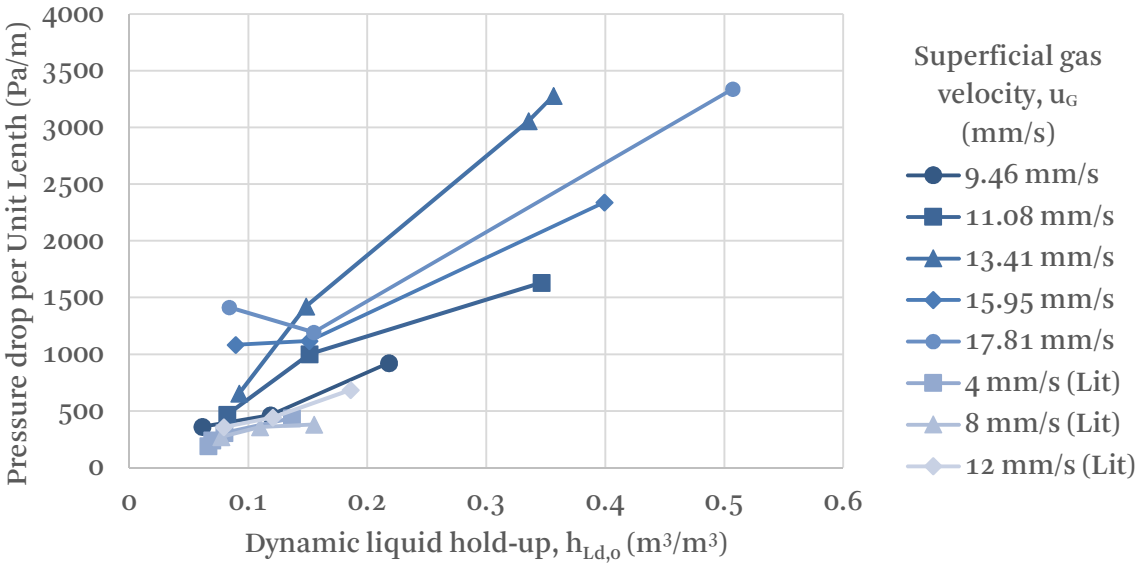


Figure 5- 12: Wet pressure drop vs. dynamic liquid hold-up below the flooding point. Includes literature values for water and Raschig rings at the same operating conditions. (76)

The experimental data can be seen to mostly follow an increasing trend with an increased superficial gas velocity, except for the 13.41 mm/s superficial gas velocity trend, which seems to be an outlier. The literature data shows no clear trend with increasing superficial gas velocity. With the limited data available it can be said that the literature and experimental data share very similar trends. The trends are similar in angle, showing a direct correlation between the liquid hold-up and the pressure drop over a column. The literature trends lean slightly more to the liquid hold-up side. This may be attributed to the larger surface area of the packing used in literature. It can be therefore deduced that the pressure drop measurement technique had no significant effect on the readings observed.

In Figure 5- 12 the experimental trends end at much higher values than the literature trends, depicting the higher experimentally measured pressure drop and hold-up. This depicts the difference between the systems caused by packing and liquid properties, while the similar trends show despite these differences the same phenomena were investigated is a comparable manner.

5.2.6 Flooding

Flooding has been briefly mentioned in the preceding two sections, but has yet to be fully discussed. In the investigation of literature in Section 2.2.4, it was found that a multitude of definitions describing flooding is found in literature.

Stockfleth, et al. (13), being the main literature source used for comparison in this study, defines flooding as when a height of 50 mm of liquid above the packing forms. In the experimental data a liquid level of 15 mm above the column packing could be confirmed, but it was seen that the column was still hydrodynamically operable at this liquid level.

Comparing the gathered pressure drop data to the classic definition of flooding (4) as yielding an infinite pressure drop, it can be seen that the pressure drop does not tend to infinity. It was however noted that the pressure drop seemed to reach a maximum value at certain gas/liquid rates, after which the majority of liquid fed to the column was found in the column overheads. The liquid hold-up at this point also sharply increased. Taking all these phenomena into account it can be said that the column is hydrodynamically inoperable, as can be seen in Figure 5- 13, correlating to an operational flooding point in this state.

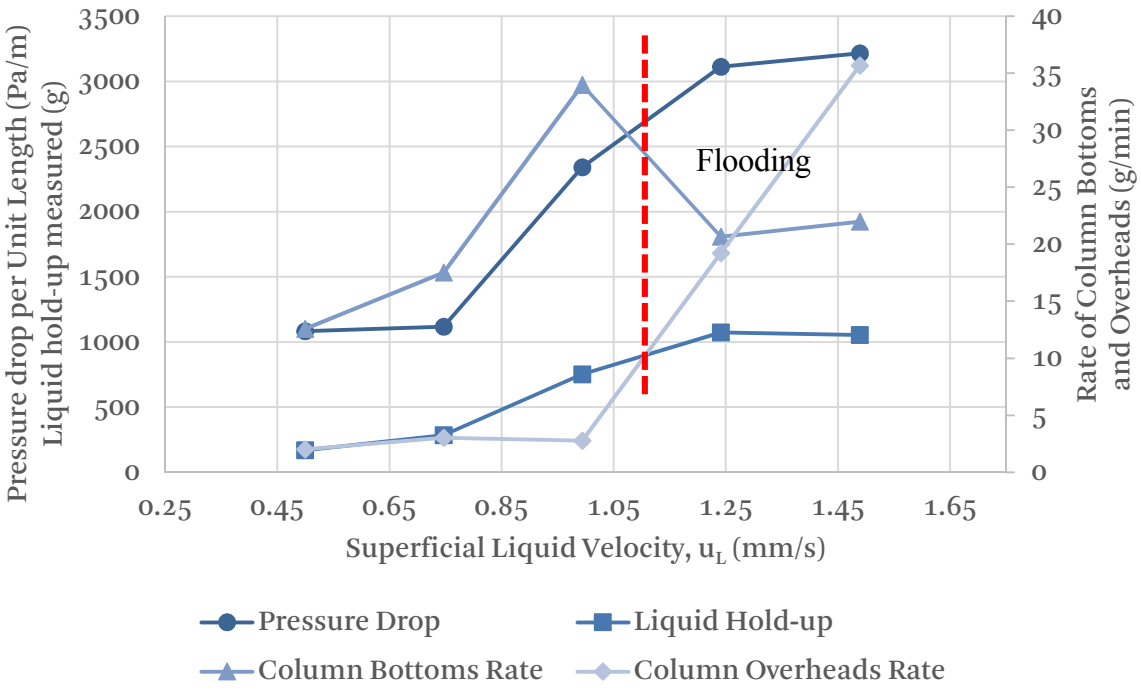


Figure 5- 13: Pressure drop, dynamic liquid hold- up and average column bottoms and overheads rate vs. superficial liquid velocity for a superficial gas velocity of 11.08 mm/s.

Flooding is thus defined for this study as total hydrodynamic inoperability of the column, and is determined by looking at several parameters of the system together, being the rate of overheads, column bottoms and liquid hold-up.

5.2.7 Entrainment

As stated in Section 4.2.6, overall entrainment is not likely to occur in the column, due to a sintered metal demister catching and returning entrained drops at the top of the column, although local entrainment may still occur in the packing bulk. To determine if overall entrainment occurred, column overhead liquid rates below the flooding point are investigated and compared to literature. If the overhead liquid rates contain entrainment, the experimental values obtained should be significantly larger than the values predicted by literature.

The calculated overhead liquid fraction for the pilot plant runs can be seen in Figure 5- 14 along with phase equilibrium literature data. It can be seen that the pilot plant overhead fractions compare well to literature data. As the fractions calculated from the pilot plant data concurs with literature data it can be safely assumed no significant entrainment occurred below the flooding point.

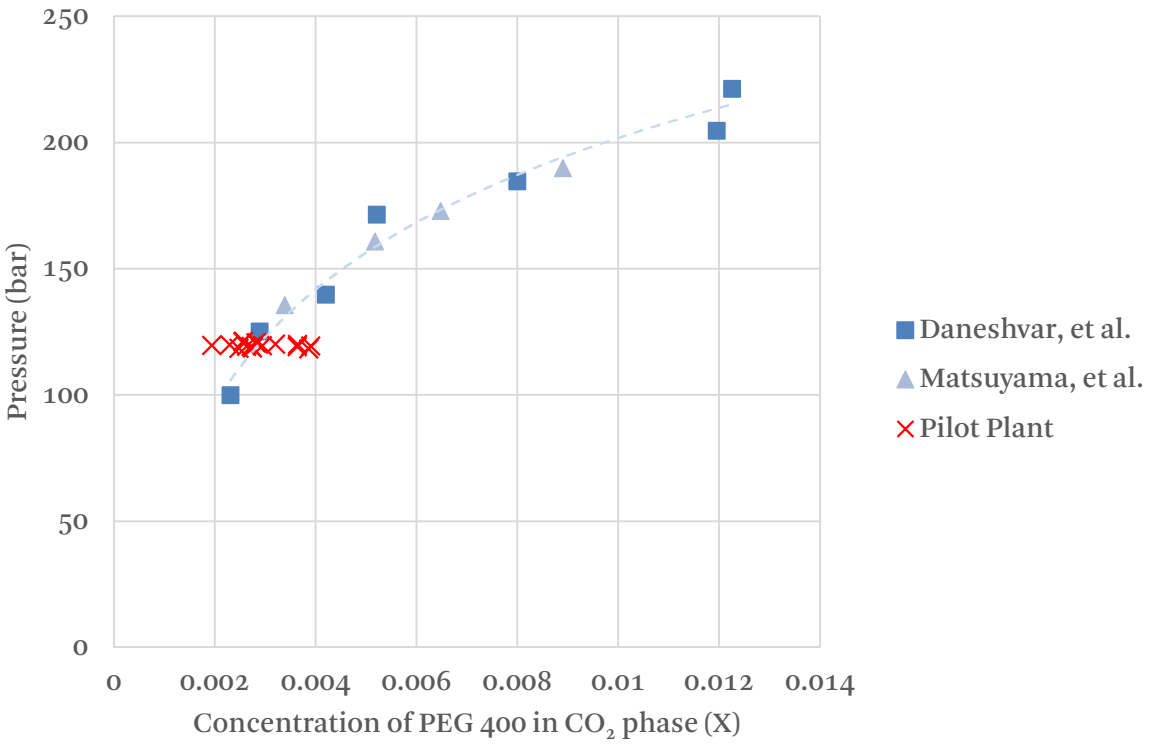


Figure 5- 14: Comparison of the measured pilot plant PEG fraction in overheads to literature. Literature data points are from Daneshvar, et al. (98) and Matsuyama, et al. (99).

5.2.8 Comparisons with Literature

As very limited literature is available for comparison, as discussed in Section 2.3, no significant comparisons could be made. Experimental data was compared with the literature data presented by Stockfleth, et al. (13), where possible. It was found that the experimentally determined data differed significantly from the literature data. This can be ascribed to:

- Differences in the column diameter and packing type. The packing type will have an especially large influence. Literature available uses a solid glass raschig ring, while a knit mesh packing random packing is used in experiments. The raschig rings used are also much smaller in diameter and possesses a much larger surface area.
- Differences in operating fluids. PEG and water will not behave the same in a supercritical fluid. Water is strongly polar, while the PEG molecule, being a polymer, exhibits much less polarity. Further the PEG 400 viscosity under supercritical conditions is smaller by a factor of ten.
- The influence of mass transfer. Water has a significant solubility in Supercritical CO_2 Stockfleth attempts to negate this by mixing the phases in an autoclave before pumping them into the supercritical column. The current study selected a system that has almost

negligible solubility in the supercritical phase and mathematically adjusts for the influence of the solubility in the liquid phase.

- Differences in experimental method. One such difference is the determination of the pressure drop over the column.

5.3 System Verification and Repeatability

5.3.1 Physical Verification

Several tests were performed to verify the pilot plant. The pilot plant was tested with only CO_2 up to a pressure of 290 bar and 180°C. No leaks or mechanical failures occurred after 8 hours of running at these extreme conditions.

5.3.2 Hydrodynamic Data Repeatability

In terms of verifying the experimental data, three experimental runs were performed at the same experimental conditions. It was found that the data obtained from these runs correlated well. Seen below in Figure 5- 15 is the comparison of three pressure drop trends acquired at.

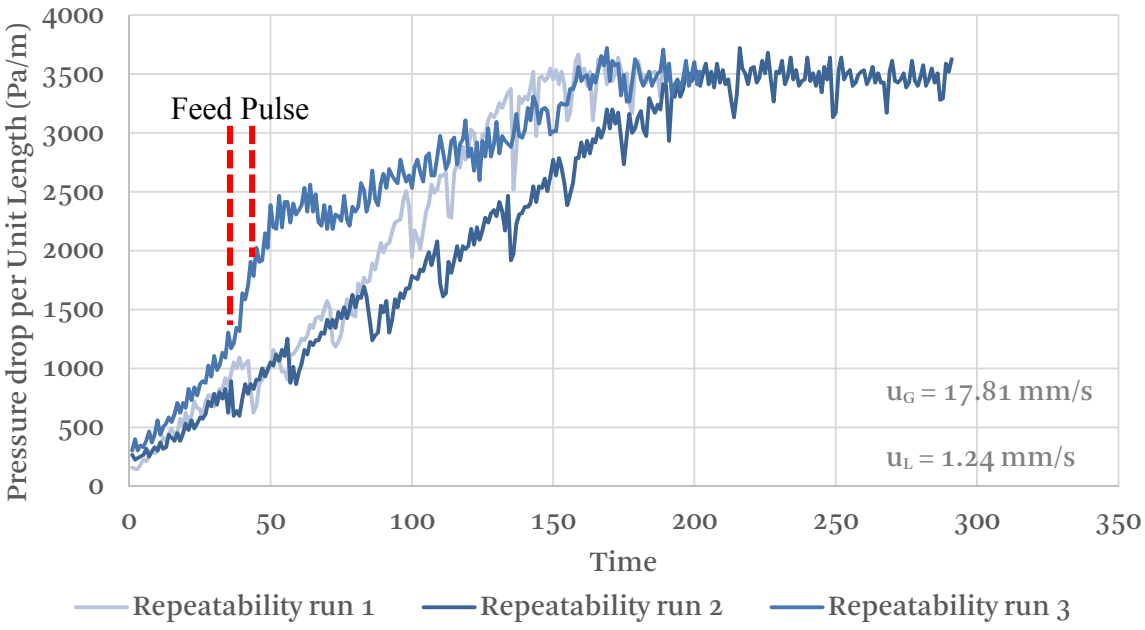


Figure 5- 15: Plot of repeatability runs wet pressure drop, including disturbance in run 3.

All the runs yielded the same approximate pressure drop, although it is important to note that the time to reach equilibrium differs somewhat. A disturbance was also introduced in run 3, in the form of a short pulse of a doubled liquid feed rate. It is seen that the system, despite the pulse, still attains the same equilibrium and liquid hold-up.

6. Conclusions

The conclusions of this study are divided into three parts, being conclusions from literature, establishment of a supercritical pilot plant and the measurement of reliable hydrodynamics under supercritical conditions. The first section gives a broad overview of important points from the literature conclusion, Section 2.7. The second section discusses the procedure followed in establishing a new pilot plant and the design goals achieved. The final section draws conclusions from the experimental section of the work.

6.1 Conclusions from Literature

After covering basic background literature, a thorough literature survey of hydrodynamics under supercritical conditions was performed. It was found that limited work on this topic is available.

The available literature data concerning hydrodynamics under supercritical conditions is found lacking in several departments, firstly only covering a small range of fluid properties, both liquid and supercritical. Secondly only a limited amount of packings are covered, with systems operating with random packing found to be lacking in particular. Additionally, previous studies use systems where significant mutual solubility is possible, causing mass transfer to become an issue.

Concerning the modelling of hydrodynamics under supercritical conditions further conclusions were drawn. It is noted from literature that firstly, hydrodynamics under supercritical conditions are not readily predicted by models applicable at normal and vacuum pressures and secondly, that hydrodynamics under supercritical conditions are not fundamentally different from atmospheric hydrodynamics. Despite this no universal correlations are available that can predict hydrodynamics, especially flooding, under supercritical conditions.

The lack of data and shortcomings in literature forces industry to rely on pilot plant studies for data, decreasing the attractiveness of the technology. In order to remedy the shortcomings in literature it is concluded that supercritical hydrodynamic pilot plant data is to be collected.

6.2 Establishment of a Supercritical Pilot Plant

As no facility with sufficient capabilities was available at the time, different pilot plant options were investigated. Ultimately it was decided to decommission an existing pilot plant, which has become unused and outdated, and build a new pilot plant, salvaging major equipment from the previous plant to keep costs down. This laid the groundwork for a new pilot plant tailored to meet the needs of this study. The pilot plant was designed with future work and possible expansion in mind, leading to a robust solution.

A plant process was conceptualized and developed into a detailed design. Concurrently the previously existing pilot plant was dismantled and all the major pieces of equipment cleaned and serviced in preparation for reuse. After a detailed design the pilot plant was constructed and tested. A digital logging and control system (HMI & PLC) was designed and programmed with partial assistance from Ateka Automation. All sensors were tested against known states and calibrated in the PLC system. Operating and safety procedures, including a full HAZOP, were established and tested.

It was found that the plant could safely withstand the design pressures and temperatures and consistently measure the required hydrodynamic data. The plant conforms to current governmental pressure certification and pressure safety regulations.

6.3 Measurement of Reliable Hydrodynamic Data

With regard to experimental work the first task was selecting appropriate systems. Several packings were identified and procured with 1/4" Dixon rings selected for the initial experiments. CO_2 was selected as the supercritical fluid of choice, being the most common supercritical solvent, easy to acquire, cheap and non-toxic.

A liquid phase with low solubility in the supercritical phase, in this case CO_2, was required. Literature showed that polyethylene glycol or PEG is a good option for initial testing. PEG 400 was selected and procured from Merck chemicals. After selecting 313.15K (40°C) and 120 bar as the operating conditions for initial experiments, the properties of the selected fluids were determined.

A problem with the DP cell pressure reading was identified and, after investigation, attributed to a denser CO_2 phase forming in the capillaries leading to the sensor. A fixed sensor offset value of 2360 Pa is determined and applied to all experimental pressure drop readings.

Experiments with PEG 400 were performed at five different solvent flow rates, each with at least five different liquid flow rates. It was found that with increasing gas or solvent flow rate the

liquid hold-up and pressure drop increases, up to the flooding point. After the flooding point the pressure drop and liquid hold-up reaches a shared maximum value, staying more or less constant with increasing liquid or gas flow rate. A new parameter for dry pressure drop was regressed, with the friction factor, ψ , found to be independent of the gaseous Reynolds number, Re_G , contrary to literature. Flooding conditions were identified using an overall view of the system, and defined as where the system becomes totally inoperable. Comparison with literature yielded mixed results, but differences could be explained by differences between the experimental systems. By plotting the interdependent pressure drop and liquid hold-up for both experimental and literature values acceptable correlation was found between the two systems.

7. Recommendations

This study was primarily focussed on the construction and verification of the pilot plant. Now that the pilot plant is ready there is a multitude of future applications to recommend. Some of these general recommendations are:

1. Further hydrodynamic studies, measuring a wider range of packings for a broader range of fluid properties.
   - 1.1 Additional packings not used in this study have already been acquired and can be tested with minimal effort.
   - 1.2 Further un-investigated fluid properties include the liquid viscosity and liquid surface tension.
   - 1.3 Investigate the effect of the gaseous viscosity on hydrodynamics.
   - 1.4 Only CO_2 has been used in supercritical hydrodynamic studies. Different supercritical fluids will allow for a wider range of system properties, leading to a more robust model if the data is ever fitted to a correlation.
   - 1.5 Experiments with even less soluble liquids like Polytetrahydrofuran (PTHF) should yield more accurate hydrodynamic data.
   - 1.6 The testing of atmospheric hydrodynamics in the pilot plant to serve as comparison with the measured hydrodynamics under supercritical conditions.
2. The fitting of the gathered hydrodynamic data to semi-empirical or empirical correlations to provide a generalized prediction of hydrodynamics under supercritical conditions.
3. The plotting of flooding data gathered in further studies in terms of the flow capacity factor and liquid load to present a flooding diagram type solution.
4. A numerical or computer model of the column hydrodynamics developed in-house. No computer modelling has been performed on supercritical columns with random packing.
5. Industry oriented extractions and pilot plant studies such as natural extracts and tailored separations.
6. Most industrially available supercritical pilot plants seem to focus on solid extraction. The addition of a solid extractor vessel would increase the usefulness of the pilot plant. The current feed vessel is made for high pressure application and can easily be modified to serve as a solid extraction vessel. This can be done in conjunction with Recommendation 13.

Recommendations pertaining directly to this project:

7. The capillaries leading to the DP cell are unheated and exposed to room temperature. This caused a dense CO_2 phase to form in the capillaries, affecting the pressure drop reading. It is advised that diaphragm seals are installed on the capillaries, at the column to avoid this effect. Failing this the capillaries can be heated to a temperature close to the column operating temperature to somewhat negate this effect.
8. The decanting of the column bottoms has been proven to disturb the column equilibrium. It is advised that a high pressure vessel of approximately 2 litres be constructed and attached to the bottom of the columns. This vessel can then be used to catch the column bottoms. In the case of measuring liquid hold–up a valve between the column and the vessel can be closed to allow the liquid hold-up to collect in the column without mixing with the column bottoms. This will provide a more accurate way to measure the liquid hold–up, as the chances of bottoms affecting the results are greatly reduced. A concept sketch of the idea can be viewed in Figure 7- 1.

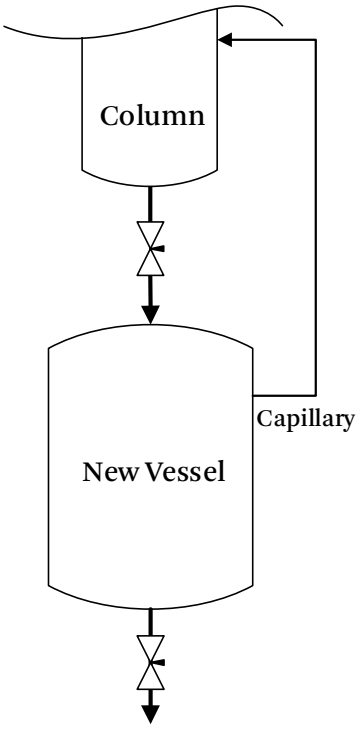


Figure 7- 1: Bottoms tank rough concept sketch.

9. NV 4-1 was used to choke the overhead product to provide a more stable column pressure. This proved less reliable at low solvent flow rates. This can be improved by replacing the needle valve with a regulating valve.

10. The installation an additional temperature probe(s) on column C 3- 2, specifically on the middle to bottom section of the column. This will provide a better insight of the column interior and provide information as to any possible temperature gradients.
11. The heaters H1 and H2 were unreliable during experimentation, regularly over or under heating, leading to longer waiting times. It is advised that the control systems on these boxes be serviced or replaced.
12. To further aid equilibrium the pulsing effect of the solvent and liquid feed pumps can be lessened by adding buffer vessels just after the respective pumps. This has to be carefully planned if implemented, as the vessels add dead volume to the system which may affect readings and measurements.
13. At low flow rates the liquid feed pump sometimes struggled to keep itself primed, leading to a loss in flow through the pump. In order to remedy this air pressure was applied to the feed vessel. Further, for high flow rates the feed tank had to be refilled several times taking the focus away from monitoring the pilot plant. It is recommended that a new, bigger feed vessel is installed on the second floor to provide the needed pressure head and liquid volume to remedy this problem.
14. In retrospect PEG 400 did not prove to be the ideal initial testing fluid due to the high solubility of CO_2 into the liquid phase. It was possible to compensate for this in experiments, but it is advised that in future that bubble and cloud point data of a selected binary system is determined beforehand to identify a system with low mutual solubility.

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Appendix A: Existing Pilot Plant Literature

The information obtained from various sources concerning pilot plants are gathered in this section. The order of appearance is as follows:

A.1 University of Stellenbosch

A 1.1 Fractionation Pilot Plant – (Unavailable for experimentation)

Experimental Setup

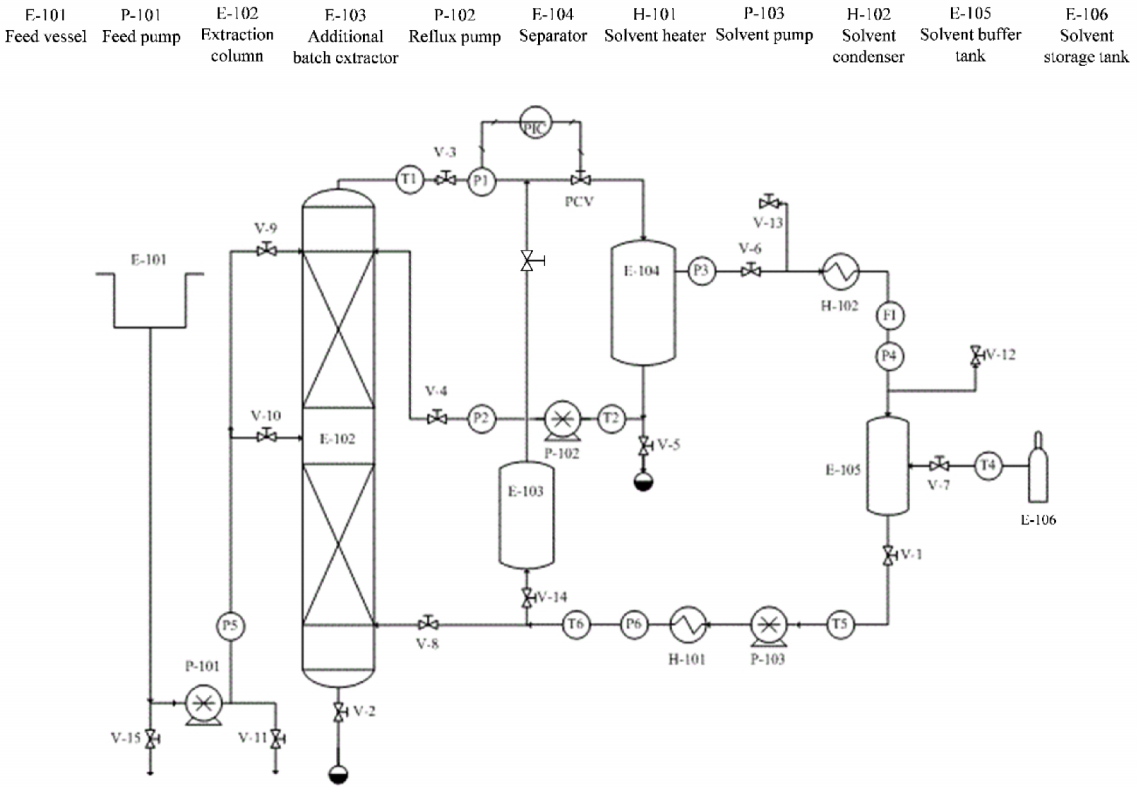


Figure A- 1: P&ID of the unavailable University Stellenbosch SFF pilot plant setup.

The following plant description is found in-house at the Department of Process Engineering, University of Stellenbosch:

Feed

The feed vessel (E- 101) is an 8 liter open top stainless steel vessel with a copper coil on the inside, through which heating fluid is circulated. The feed mixture flows downwards to the feed pump (P- 101) inlet. The feed pump is a variable stroke length diaphragm pump with a maximum rating of 2 liter/hour at 26.0 MPa. The discharge side of the pump is connected to two possible outlets. If V- 9 is open (and V- 10 closed), the feed is pumped to the top of the column, and if V- 10 is open (and V- 9 closed) the feed enters the column in the middle. There are two valves located at the bottom of the feed lines, V- 15 and V11, which can be used to drain the feed lines and feed vessel after an experimental run.

Fractionation/Extraction

In the fractionation column (E- 102) the solvent flows counter current to the feed mixture and selectively dissolves certain compounds. The column is 0.028 m in diameter and consists of two 2.16 m high sections of Sulzer DX packing. Sulzer DX packing is a gauze type structured packing woven from stainless steel wire. The specifications of Sulzer DX structured packing are given in Table A- 1.

The column has a maximum operating pressure of 30.0 MPa and maximum operating temperature of 420 K. The column is jacketed and heated with circulating fluid. The solute feed mixture enters the column, either at the top or in the middle. The feed line protrudes to the center of the column, providing a single drip point. Crause (37) showed that this is sufficient for a column of this diameter, to wet the entire packing section. At the bottom of the column there is a sight glass to allow one to observe the liquid level of the bottoms product that accumulates here. The bottoms product can be removed through V- 2.

Table A- 1: Geometrics of Sulzer DX packing.

Geometric information	Value
Crimp height (mm)	3
Channel base (mm)	6.5
Channel side (mm)	4.4
Surface area (not including column wall area of 140 m^2/m^3) (m^2/m^3)	900
Void fraction (%)	77
Channel angle with horizontal (°)	60

The pilot plant setup can also be operated in batch mode, usually for the extraction of compounds from solid feed matrices. The batch extractor vessel (E- 103) is then used, instead of the fractionation column. No details are provided for operation in this mode since it will not be implemented during this investigation.

Separation

When the solvent, loaded with extracted compounds, exits the fractionation column it expands over a pressure control valve (PCV), and flows into the separator vessel (E104). The separator is operated at the solvent vapor pressure in the solvent storage tank (E- 106) (which varies slightly with ambient temperature). The separator is equipped with Goodloe knitted packing at the top, which acts as a demister device to aid in the coagulation and droplet formation of the extracted compounds. The separator vessel is also equipped with a sight glass to allow the manual

monitoring of the extract product liquid level. The extract product can be withdrawn through V- 5. The separator vessel is kept at a temperature slightly higher than the operating temperature of the column with a jacket that holds circulating heating fluid.

If reflux is employed, a fraction of the extracted product is pumped back to the top of the column. The reflux pump (P- 102) is a double diaphragm pump with an adjustable stroke length. The maximum capacity of the pump is 8 liters/hour and the maximum discharge pressure is 30.0 MPa. Reflux was not utilized during this investigation.

Solvent regeneration

The solvent that exits the separator is condensed in a heat exchanger (H- 102) and flows through a mass flow meter (F1) into the solvent buffer vessel (E- 105). The solvent condenser consists of two sections, one cooled by cooling water, and the other with chilled propylene glycol water. The solvent condenser and buffer vessel operates at the solvent vapor pressure. The buffer vessel feeds the solvent pump (P- 103) and is cooled down to ensure that the solvent provides enough head to the pump. Additional solvent is fed to the buffer vessel from the solvent storage tank (E- 106). The solvent pump is a variable stroke length diaphragm pump with a maximum rating of 29 liters/hour at 26.0 MPa. On the discharge side of the solvent pump, the solvent is heated with a heat exchanger (H101) to reach the column operating temperature. The solvent enters the fractionation column at the bottom, flows upward, exits at the top, unloads extracted solutes in the separator, and then goes through the entire regeneration cycle again.

Most of the solvent is recycled during an experimental run, but there are some losses to the atmosphere when the extract and bottoms products are withdrawn periodically. By keeping the feed line from the solvent storage tank to the solvent buffer tank open during operation, the lost solvent is replaced in the system.

Utilities

Two heaters provided the heating fluid to heat up the vessels and pipelines. The heating fluid circulates through copper trace heating lines, as well as through the heating jackets of the fractionation column and separator vessel. One heater was mainly used to heat the column, while the other heater was usually set to a slightly higher temperature and used to heat the feed vessel, solvent inlet to the column and the separator vessel.

An industrial water chiller was used to supply chilled water (containing propylene glycol) to the solvent condenser and buffer vessel. It was also used to trace the line that feeds the solvent pump to prevent vaporization in the line, which can lead to cavitation in the pump.

A 1.2 SITEC–Sieber Pilot Plant

Experimental Setup

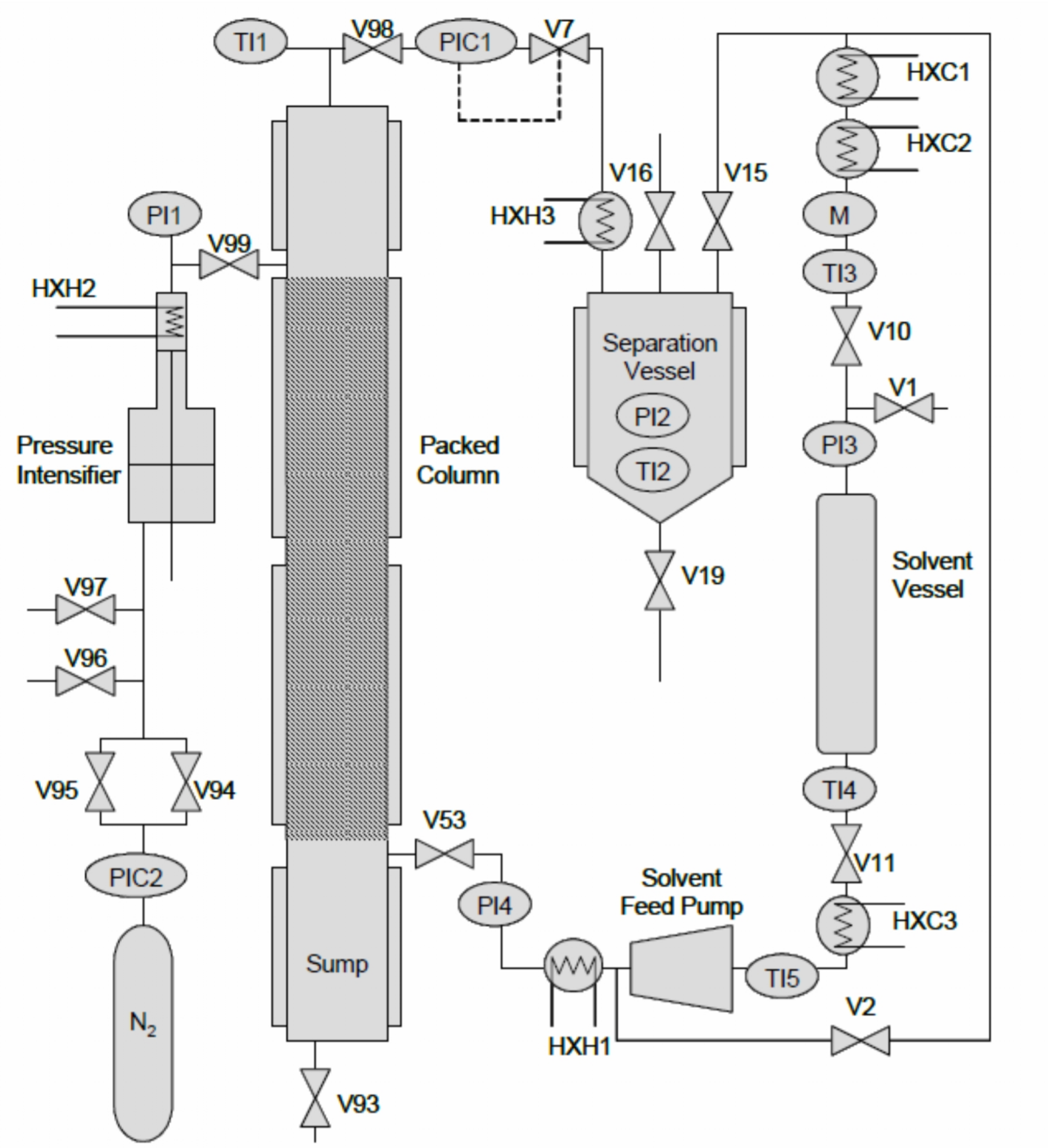


Figure A- 2: P&ID of the SITEC-Sieber University Stellenbosch SFF pilot plant setup (22).

Plant Description:

The following plant description is found in the masters script of Schwarz (22).

An existing pilot plant set- up, designed by Sieber- Sitec, Switzerland, and provided by SASOL, is used and modified to be suitable for use in this work. A counter- current set- up with no reflux is used.

The core of the pilot plant is a 4.3 m tall 0.017 m inner diameter extraction column with a packing height of 3.5m (0.5 m sump and 0.3 m overheads clearance). The column is constructed with 1" outer diameter medium pressure stainless steel tubing, as provided by Autoclave Engineers, and filled with Pro- Pac distillation packing (316SS from Aldrich, catalogue number Z210552). The wax feed is introduced at the top of the column with the aid of a 600 mL pressure intensifier, driven by nitrogen pressure (area ratio of 24.6). The wax is melted in the pressure intensifier and introduced as a liquid at column temperature.

The solvent cycle on the original pilot plant is used. Liquid propane is stored in the solvent storage tank (the pressure equivalent to the vapor pressure at atmospheric temperature), and after supercooling is fed to a diaphragm- metering pump, where it is pumped, in the liquid form, to the column pressure. After heating to supercritical conditions at the column temperature, the solvent is introduced at the bottom of the column. The solvent proceeds up the column and the loaded solvent then exists the column at the top and proceeds via a pressure regulating valve and heater into the separation vessel. The separation vessel is operated at the solvent storage pressure and the wax is allowed to separate from the solvent. The solvent now proceeds through, first a water cooler and then a refrigeration system and back into the solvent storage tank - makeup solvent may be required and is added to the system at the top of the storage tank. In order to facilitate start- up a solvent recycle stream is used.

At the bottom of the column a 0.5 m long, 0.017 m inner diameter storage tank (sump) at column pressure allows for a limited quantity of bottoms product to be stored, which can be periodically removed. The overheads product is removed periodically from the bottom of the separation vessel.

A.2 The University of Texas at Austin

Experimental Setup

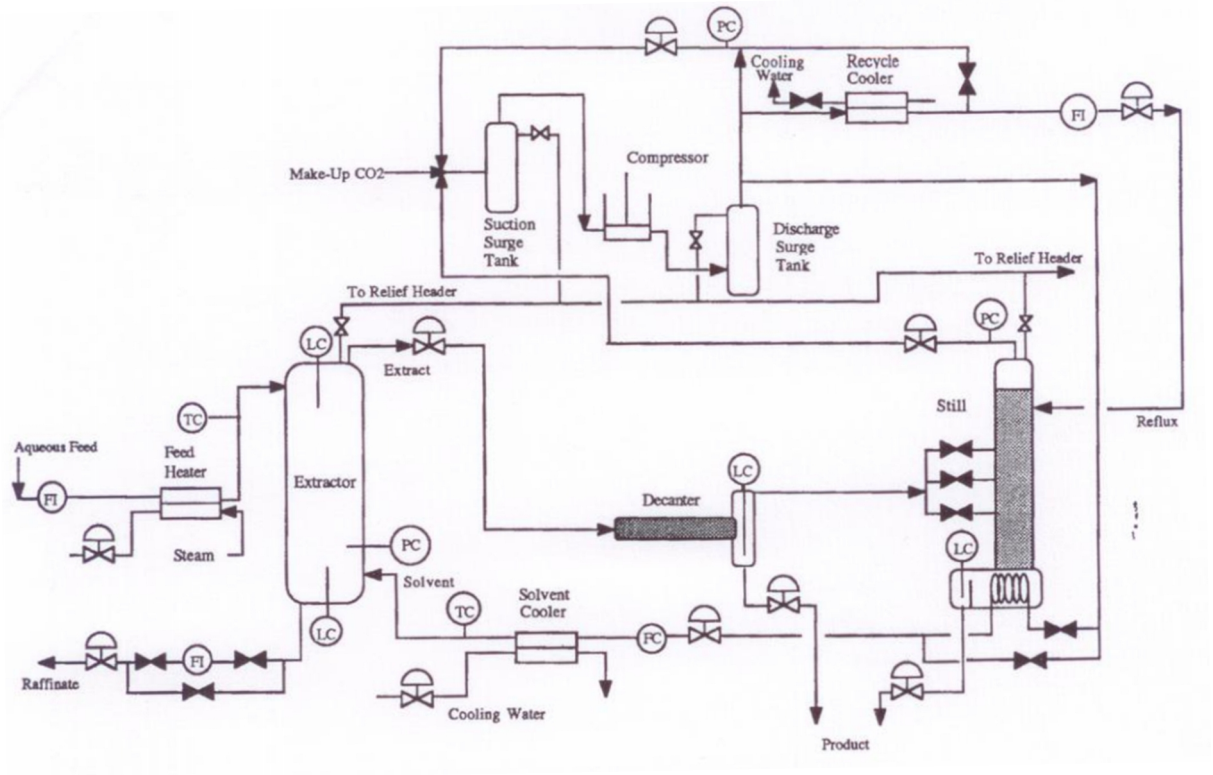


Figure A- 3: P&ID of the equipment used by Seibert and Moosberg (10).

Plant Description:

The following description is typed over as is from the original journal article by Seibert and Moosberg (10):

The stainless steel extraction column was 9.88 cm in diameter (i.d.) with a total height of 215 cm. The column contained 32 high pressure glass windows to allow viewing of the contacting action inside. The windowed extractor was rated to 102 atm. In some cases, data were obtained from an identical column without windows, which was rated to 205 atm. The dispersed phase was distributed with a crossed ring sparger containing nine 0.47 cm diameter holes spaced uniformly to ensure equal distribution. The continuous phase was distributed with an "L"-shaped sparger containing 15 0.32 cm holes. The containing distance between distributors was 168 cm.

The pilot plant was controlled with a distributed control system. Process flow, pressure, steam and cooling water valves were controlled pneumatically. The liquid feed was delivered to the extractor with two positive displacement pumps operated in parallel. A dampener was used in the liquid feed line to prevent flow pulsation. The solvent was delivered to the extractor with a

reciprocating compressor. Mass flows of the liquid feed, raffinate, and solvent were measured to a high degree of accuracy using Micro-Motion mass flow meters.

Pressures were measured with standard pressure transducers. These transducers were located on the discharge of the compressor, extractor, and solvent fractionator. All vessels contained relief valves which were piped to a common relief header.

The interface level was controlled with a capacitance probe and manipulation of the raffinate flow rate. Likewise, the solvent fractionator and decanter liquid levels were controlled with capacitance probes. The temperatures of the feed and solvent entering the extractor were measured with thermocouples and controlled by heat exchange with cooling water or steam. The compressor recycle stream temperature was controlled in a similar manner.

Analysis of all streams was performed with two online gas chromatographs utilizing thermal conductivity detectors. The samples were collected at process conditions and transferred in 0.318 cm (o.d.) stainless steel tubing to a two microliter sampling loop using a six-port manual sampling valve. This arrangement prevented two-phase sampling and yielded excellent reproducibilities.

A.3 Technical University of Hamburg, Harburg

Experimental Setup

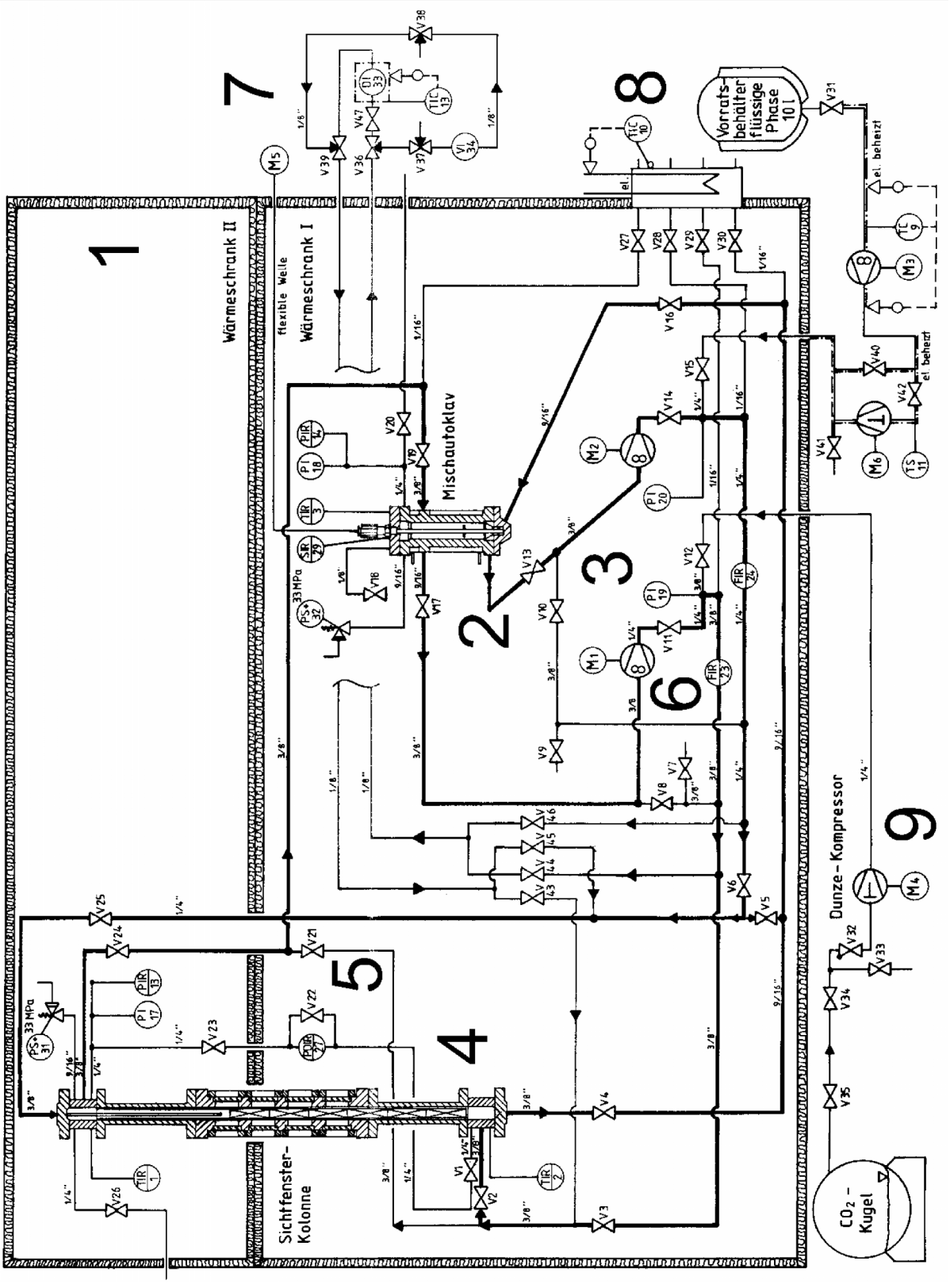


Figure A- 4: P&ID of the equipment used by Stockfleth, et al. (14; 13) and Budich, et al. (71; 72).

Plant Description:

The following description is translated from the original German in the Ph.D. dissertation of Stockfleth (76):

This system can be operated at a maximum operating pressure of 36.5 MPa and a temperature of 393 K. The facility is divided into a hot zone, which is the area in the heating chamber [1] and a cold area, which is the area outside of the ovens. Peripherals and sensitive electronics are located in cold area during the actual pilot plant located in the hot area. The two phases are loaded into the equilibrium autoclave (Mischautoklaven) [2]. From there they are fed with high-pressure gear pumps [3] to the high pressure window column [4]. The column is operated in a countercurrent manner, with the liquid collecting in the bottom and recycled to the equilibrium autoclave and the gas leaving the column via the top back to the equilibrium autoclave. During the flow through the column, the pressure drop is measured with the pressure transducer [5] and the respective mass flow rates are detected with the mass flow meter [6]. In the cold area there is a density meter [7], which is heated with a heating bath. Both the gas and the liquid stream may be selected from the valves V43- V46 are redirected to the density meter. Before the test, the liquid feed is loaded into the reservoir [8] in the cold zone. This is a double- walled glass vessel and can be heated with a thermostat. The feed line to the gear pump, which pumps the liquid into the pilot plant, is also heated. The purpose of these heaters is to lower the viscosity of viscous liquids, or to liquefy experimental materials which are in a solid state at room temperature. The pressure in the pilot plant is produced by carbon dioxide with a two- stage compressor [9].

A.4 SITECH- Sieber Engineering AG

Experimental Setup

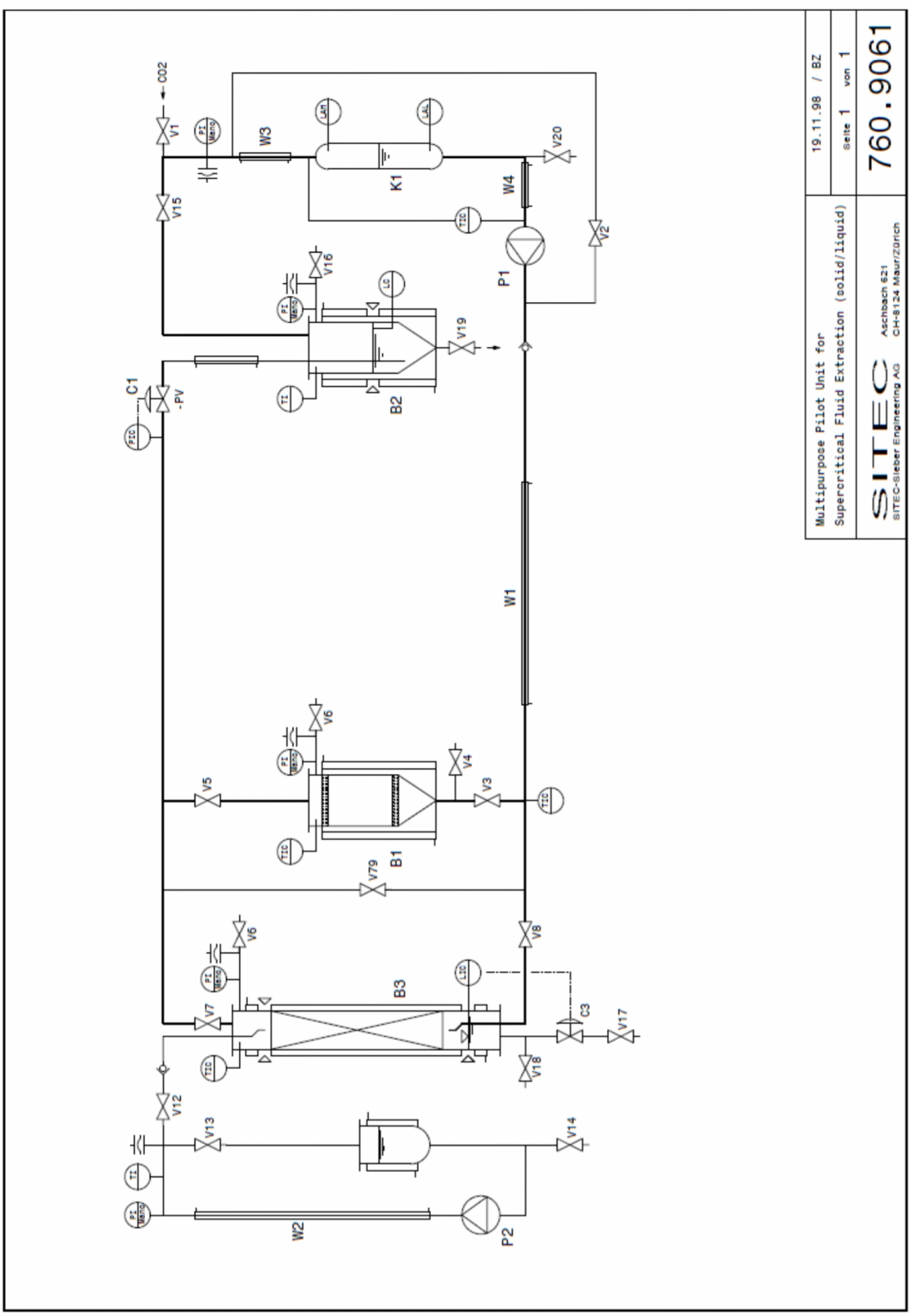


Figure A- 5: P&ID of a multipurpose pilot plant, model 101- 300- AFF.
As recommended by SITECH- Sieber.

During e-mail correspondence, as can be seen at the end of this section, a non-binding price of CHF 262 600 or ZAR 3 240 000 is quoted. The following description and details section was received from SITECH-Sieber and typed over as is:

Process

This turn- key multipurpose Pilot Unit for the extraction with supercritical gases is built for the following operating conditions:

Solvent:	Carbon Dioxide or any other non inflammable gas which may be liquefied under similar conditions.
Extraction Pressure:	75 - 300 bar
Extraction Temperature:	ambient - 200°C (higher temperatures optional)
Separation Pressure:	50 - 60 bar depending on storage bottle pressure (higher pressures optional)
Separation Temperature:	ambient - 60°C

The Pilot Unit may be operated continuously, extracting solutes from liquid raw material or in the batch mode extracting solutes from solid raw material.

The high capacity diaphragm metering pump delivers a contaminant free supercritical fluid to the extraction vessel. The pump capacity is adjustable from 15 - 100 %. The fluid has already reached extraction conditions when entering the column, wherein the temperature is kept constant up to the outlet by the jacket heating.

The liquid raw material is pumped into the column through an upper connector from where it drops to the bottom in counter flow with the up streaming supercritical solvent fluid. The residue is collected at the bottom of the column and is automatically discharged at a rate controlled by the level controller. The extract on the other hand is carried over to the separator by the supercritical gas.

Before entering the separation vessel the pressure is reduced by a control valve lowering the solvent power of the carrier gas to practically zero. There are three distinct phases entering the separation vessel: liquid CO_2, gaseous CO_2, and the extract. The extract drops to the bottom of the separation vessel from where it is collected and removed through a hand valve. In the separation vessel a liquid level is maintained to improve the separation of the extract. The entering liquid CO_2 is evaporated continuously at moderate temperature.

In the condenser the gas is condensed and in the following metering pump the supercritical solvent fluid is brought up to the chosen extraction pressure. In the downstream heat exchanger the solvent fluid is heated up to the required extraction temperature which means that the solvent fluid has reached the extraction conditions when entering the column through the bottom connector.

Flowing up the column in counter flow with the injected liquid raw material from the top, additional extract is dissolved continuously and the closed loop cycle continues. To extract solutes from solid raw material the pilot unit is operated in the batch mode. The solid raw material is introduced into the extractor in a cylindrical basket with filter elements at both ends. These filter elements retain the raw material but are permeable for the solvent fluid and

the dissolved extract. As in the process with liquid raw material, the solvent fluid dissolves the solute as it flows upstream through the solid raw material.

The further steps of the process are the same as with liquid raw materials e.g. pressure reduction, separation, evaporation, condensing, pumping and heating, thus closing the process cycle again.

The spray nozzle, solution and dissolution may be transmitted on TV- screens or Videos through the installed standard optical windows. The phase boundaries in the separator can be observed and the liquid level is controlled.

The vessels are easily accessible and the closures are hand operated. The extract from the separator is drained manually and the residue from the bottom of the column continuously.

The temperatures are controlled by heaters; the extraction pressure by a triggered control system, which eliminates the clogging risk by the extract in the control valve seat.

For reliable scale- up and economical reasons the design of the system is based on pumping the supercritical fluid rather than compressing it in the non- relevant and costly gaseous state. Built for preparative work, the unit can also be used for screening and analytical research. For certain industries such as pharmaceuticals it can even be used as a full production unit. The capacity of this extraction unit is large enough for the production of batches for market testing.

All relevant data are indicated on digital displays on the front panel flow sheet and, as an option, may be brought up to a Personal Computer. Various options are available, such as larger vessel capacities (up to 20 litre), longer columns, higher pressures, temperatures and mass flows.

Extent of Supply

Item 1 Extraction vessel B1

Capacity:	1 litre
Insert basket:	600 ml
Operating pressure max.:	300 bar
Operating temperature max.:	200°C
Threaded quick opening closure	
Temperature measurement inside the vessel	
Heating with PID temperature control and insulation	
Connections:	Std. 1/4" HP
Materials:	AISI 316 Ti

Item 2 Column B3

Capacity:	2 litre
Internal length:	2 meter
Internal diameter:	38 mm
Max. operating pressure:	300 bar
Max. operating temperature:	200°C
Threaded closures	
Level control of bottom product	
Heating with PID temperature control and insulation	
Window and pressure connections:	

radial:	5 x 2 per level
axial:	2 on both ends
window units:	2 sets
Packing:	Sulzer CY
Connections:	Std. 1/4" HP
Materials:	AISI 316 Ti

Item 3 Separator B2

Capacity:	1.2 litre
Operating pressure max.:	100 bar
Operating temperature max.:	60°C
Threaded quick opening closure	
Temperature measurement inside the vessel	
Heating jacket and insulation	
2 optical windows	
Automatic level control	
Dip tube	
Connections:	Std. 1/4" HP
Materials:	AISI 316 Ti

Item 4 Storage tank K1 with condenser, sub- cooler and refrigeration unit

Capacity:	10 litre
Operating pressure max.:	100 bar
Operating temperature:	- 10 to +20°C

Item 5 CO_2 - Diaphragm metering pump P1

Capacity max.:	18 litre/hr with hand adjustment
Operating pressure max.:	300 bar
Electric motor:	3 x 400 V / 50 Hz
Horsepower rating:	1.35 kW

Item 6 Heat exchanger W1

Double wall tube	
Operating pressure max.:	300 bar
Operating temperature max.:	200°C

Item 7 Liquid product diaphragm metering pump P2

Capacity max.:	2 litre/hr with hand adjustment
Max. operating pressure:	300 bar
Electric motor:	3 x 400 V / 50 Hz
Horsepower rating:	0.18 kW

Item 8 Heat exchanger W2

Double wall tube	
Max. operating pressure:	300 bar
Max. operating temperature:	200°C

Item 9 Pressure control C1 of the extraction pressure by pressure transducer, PID- pressure controller with digital display and control valve system.

Item 10 Temperature control

The temperature of the injected liquid product is controlled by its heater, the rate of evaporation in the separator by the level controller.

All five temperatures, in the column, the extractor, the CO_2 heat exchanger, the separator, and the product heat exchanger are indicated by digital displays on the front panel.

Item 11 Piping (High pressure and low pressure)

The unit is completely piped up. For a convenient installation the internal lines are brought up to a connecting plate at the skid side or rear.

Materials: HP- piping AISI 316 L valves + fittings AISI 316

Item 12 Wiring

The unit is completely wired and it can be connected to a power source by an electric 5-wire cable which is included in the delivery. Check the sense of rotation of the electric motors on the first commissioning.

Item 13 Safety

5 burst disc assemblies
Thermo contactors
Pressure limiter in controller
Temperature limiters in controllers

Item 14 Testing

The unit is tested under operating conditions (CO_2) on our test stand at which occasion the customer is welcome to participate.

Item 15 Documentation

Complete instruction manual in English describing:
Commissioning and test procedure
Maintenance and fault finding
Spare parts lists and wiring diagrams
Description of components

Utilities (customer side)

Electricity:	400 V, 3 phase, 50 Hz tot. power: approx. 14 kW
CO_2 (liquid) required pressure:	50- 60 bar bottles with dip tube purity: 99,99%
Control air:	6 bar min.
Vent line	
Ambient temperature:	min. 20°C / max. 28°C

Dimensions

Width: approx.	240 cm
Height: approx.	190 cm column: approx. 300 cm
Depth: approx.	140 cm

Weight

Net: approx. 1100 kg

From: Beat Zehnder [beat.zehnder@sitec- hp.ch]
To: Franken, HH, Mnr <hhfranken@sun.ac.za>
Subject: Multi Purpose pilot unit - Documentation and Cost estimate

Dear Mr. Franken

Thanks for your inquiry! Please find attached the desired technical description and a process flow diagram of the mentioned multi- purpose unit.

The price of this unit is approx. CHF 250,000.- - . We recommend at least the option "mass-flowmeter" (+ CHF 12,600.- -) .

We hope that we could help you for the moment. Please contact us again when you need a binding quotation for such a unit.

Have a nice week- end.

Best regards,

Beat

Dr. Beat Hans ZEHNDER

SITEC- Sieber Engineering AG, Lohwisstrasse 48, CH - 8123 Ebmatingen, Switzerland

Tel.: +41 (0)44 982 1078, Fax: +41 (0)44 982 2089, e- mail: beat.zehnder@sitec- hp.ch

Homepage: www.sitec- hp.ch

A.5 SepareCo

Experimental Setup

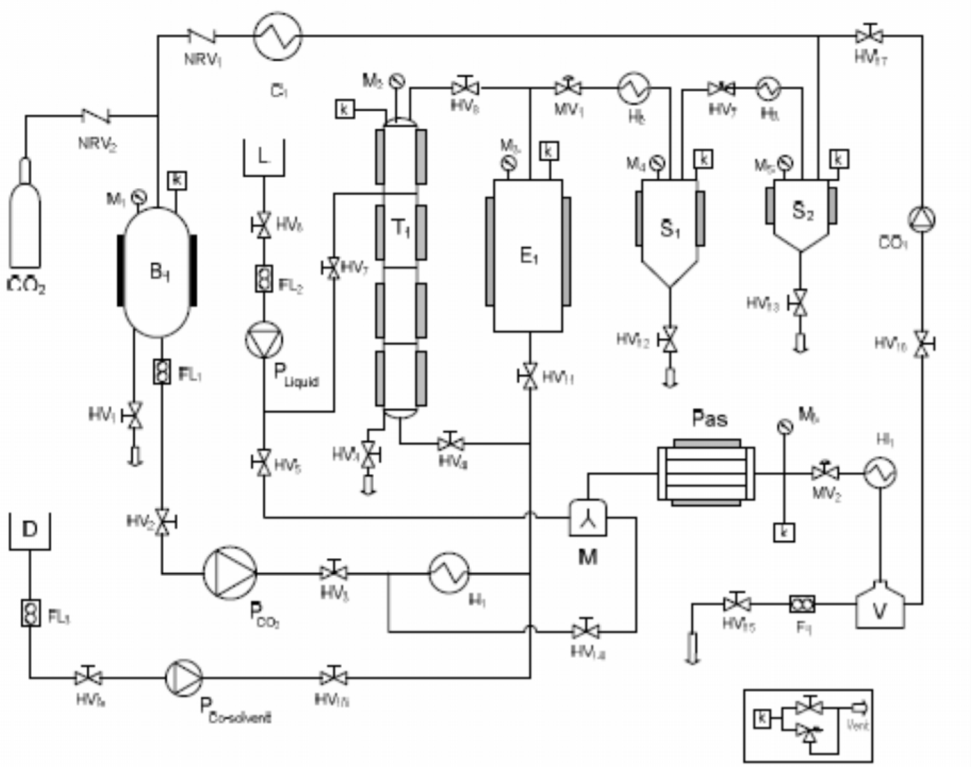


Figure A- 6: P&ID of a multipurpose pilot plant, model SCF S3W-PLC.
As recommended by SepareCo.

During e-mail correspondence, as can be seen at the end of this section, a non-binding price of EUR 360 000 or ZAR 5 220 000 is quoted. The brochure on the following pages was supplied by SepareCo.

SepareCo 2

Super Critical Fluid Equipment

SuperCriticalFluid NETWORK
The Super Critical Fluid Alliance

Supercritical CO_2 automated system

SCF S3W-PLC

Fully Automated Supercritical CO_2 Multipurpose Plant

Chemical plant are often very manual machinery. No automation, no software control is installed on board. This is not our point of view. We believe that automation is a mast in supercritical fluid plants. Thanks to automation the system configuration will change automatically from SFE to SFF or SFP (Extraction, Fractionation, Pasteurization). A trend analysis tool is included in the standard software. Illimitated process recipes.

Features

- From 3000 to 8000 ml extractor
- Super critical or liquid CO_2 extraction
- CO_2 + Co-solvent extraction
- Reverse flow CO_2 + H_2O extraction
- Fractionation tower: 300 to 700 cm
- Pasteurization reactor, 24 m
- Extractor bayonet fast closing system
- Pressure up to 550 bar
- Temperature up to 85° C
- Double separator (gravity/cyclonic)
- CO_2 reservoir/phase separator
- Liquid CO_2 floating level probe
- Pressure and temperature probes
- CO_2 membrane pump up to 60 kg/h
- Co-solvent membrane pump
- Liquid feeding membrane pump
- Electronic inverter pumps speed control
- CO_2 Coriolis mass flow meter
- Vessels safety valves (PED certified)
- Stainless steel vessels and pipes
- Electronic chiller
- Electronic boiler
- Stainless steel skid
- Liquid vacuum degassing system
- Pasteurized liquid tank
- Pasteurization buffer tank
- Dimension (cm): 370 x 235 x h:220

4 extractions mode

- Super Critical CO_2 only
- Super Critical modified CO_2
- Reverse flow
- Liquid CO_2

Fractionation Tower

Oils of vegetable or animal origin, particular categories of substances (ω-3; ω-6; etc..). The tower operates the fractionation of the oils acting in counter current with the supercritical carbon dioxide.

Pasteurization reactor

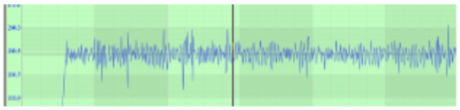
Cold pasteurization of liquids at 35° C with supercritical carbon dioxide. No heating problem with thermolabile molecules. Middle pressure treatment (85 to 120 bar).

Automation Software

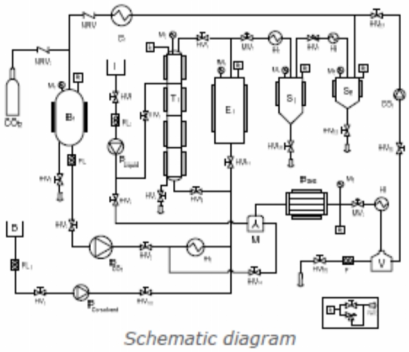
Main control screen

- Process pressure control (set-point);
- CO_2 flow rate and feeding pump flow rate;
- Electronic inverter pumps speed control;
- The temperature and pressure of each single vessel, reactor or exchanger;
- CO_2 liquid level inside the reservoir/phase separator with automatic refilling;
- Electronic boiler temperature (PID);
- Electronic chiller temperature (PID);
- Warning and emergency alarms and stop alarms;
- Temperature/pressure of each test point;
- Pumps flow rate in Kg/h or in mL/min;
- Amount of CO_2 and co-solvent or feeding liquid pumped during the cycle;
- On screen warning messages (real time and history);
- Real time graphs and trend analysis tool with limits indications;
- Process control by recipes switchable to manual;
- Full CO_2 recirculation (no CO_2 loss during the process).

Super zoomed pressure trend analysis



SCF S3W-PLC



Schematic diagram

What is a Super Critical Fluid process?

Supercritical Fluid Extraction (SFE) is the process of separating one component (the extractant) from another (the matrix) using supercritical fluids as the extracting solvent
The basic principle of SCF extraction is that the solubility of a given compound (solute) in a solvent varies with both temperature and pressure. At ambient conditions (25°C and 1 bar) the solubility of a solute in a gas is usually related directly to the vapor pressure of the solute and is generally negligible. In a SCF, however, solute solubility of up to 10 orders of magnitude greater than those predicted by ideal gas law behavior have been reported.

Classes of extracted compounds

SCF is a technology suitable for extraction and purification of a variety of compounds, particularly those that have low volatility and/or are susceptible to thermal degradation. The interest in SCFE is promoted by legal limitations of conventional solvents for food and pharmaceutical uses. The physicochemical properties of supercritical CO_2 (higher diffusivity, lower viscosity, and lower surface tension than conventional solvents) facilitate mass transfer and allow an environmentally friendly operation. Plants provide a large bank of rich, complex and highly varied structures which are unlikely to be synthesized in laboratories. Major classes of molecules include fatty acids (SCFA, MCFA, LCFA, VLCFA), terpenoids, phytosterols, alkaloids, natural phenols, polyphenols and waxes.

High pressure modifiers action

High pressure extractions of polar compounds using supercritical CO_2 followed by enhanced solvent extraction (ESE) with diverse CO_2/ethanol/H_2O solvent mixtures (0–90%, 0.5–100%, 0–95%, v/v/v), shows that this ESE solvent mixtures has a substantial effect on extracts yield and composition.

Sequential Extraction

Sequential extraction, CO_2 only followed by CO_2 + EtOH and finally CO_2 + H_2O shows different kind of fractionated extracts (Lypo » Hydro Extraction).

CAD works

SepareCo 2

Super Critical Fluid Equipment

Separeco produces and certifies all the equipment in Italy.
SEPARECO, via Rivarossa 15, PISCINA (TO) ITALY - Phone: +39 0121 33.90.47
www.separeco.com - www.separeco.it - www.scfn.eu - mail: info@separeco.com

From: info@separeco.com
To: Franken, HH, Mnr <hhfranken@sun.ac.za>
Subject: Enquiry - Supercritical Pilot Plant - University of Stellenbosch

Good afternoon Mr. Herman Franken.

Here attached please find our flayers.

The multipurpose system, 500 bar, 5 L, double pump is about 360.000 €

The tower is 4,5 m height, 4 segments (but could be designed on customer's indication from 3 to 9 meters). The internal diameter of the tower is 32 mm, as the sizing of the CO_2 pump is 36 kg/h. Packings are from Sultzer.

Delivery in 7/8 months from order.

If you need other information, we can have a phone conference by skype or similar systems.

Best regards

Separeco Srl

Dr. Claudio Colombo

Separeco Srl
Via Rivarossa, 15
10060 Piscina(TO) Italy
phone: 0039 0121 339.047
fax: 0039 0121 339.721
web: www.separeco.it
mobile telephone: 0039 348 080.76.12
Separeco is a member of the SuperCriticalFluid Network

A.6 Separex

Now flow diagram was obtained from Separex concerning their pilot plant, although a picture is available as can be seen in Figure A- 7.

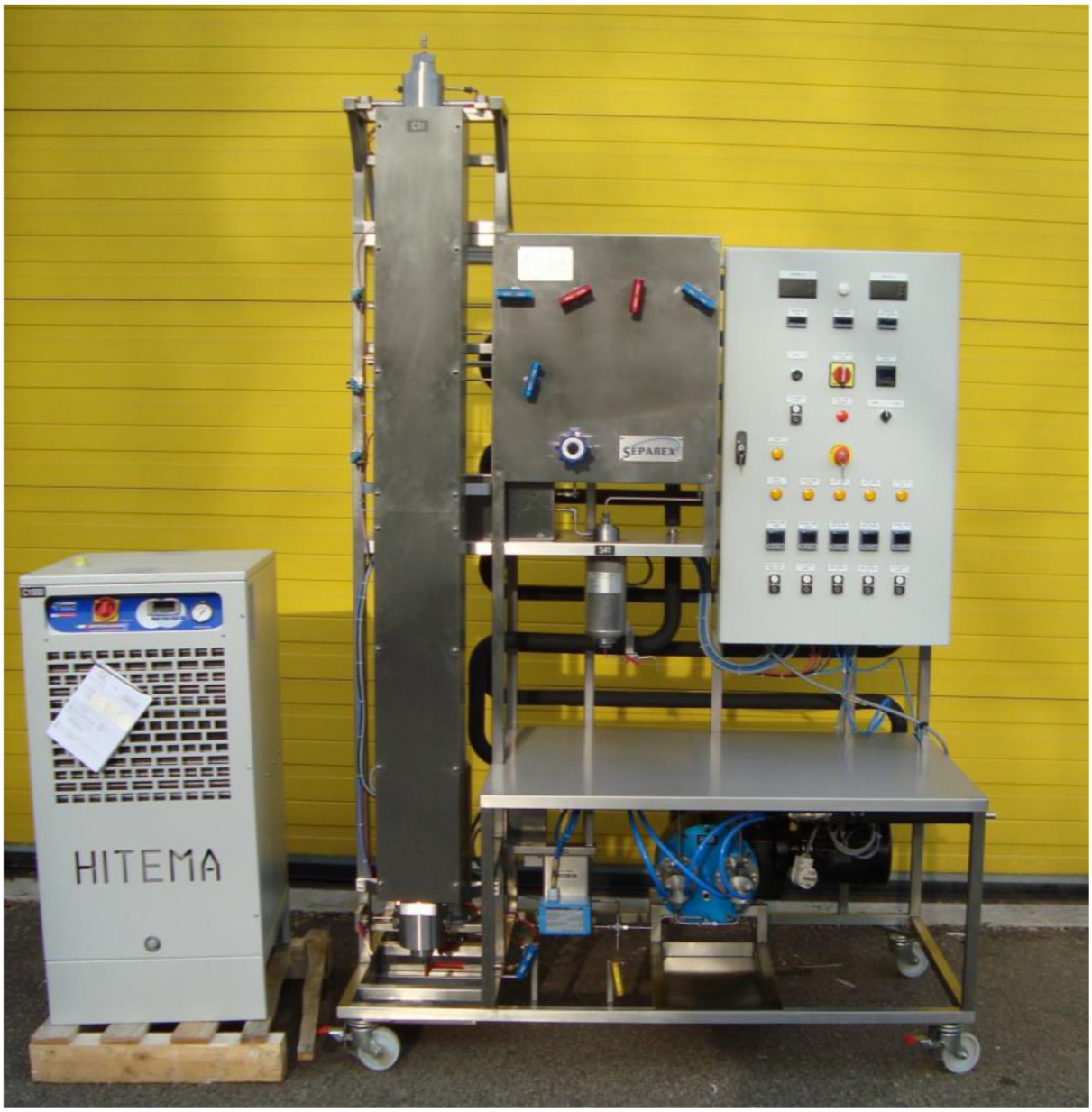


Figure A- 7: The Separex 2m extraction column.

A quote was received from Separex for EUR 96 000 or ZAR 1 392 000. Even though no process flow diagram was provided the worded description and detail in the quote document yielded valuable information.

The following description and details section was received from Separex and typed over as is:

Extraction Process Principle

CO_2 is injected in an injector close to the bottom of the column, as the feed is injected close to the top. Light extract is recovered at the top of the column and non- extracted part of the liquid (called raffinate) is recovered at the bottom.

We supply a turn key solution with a liquid feed pump and a fractionation column mounted on a skid. Column is heated with a jacket and a view port allows to control liquid level at the bottom of the column. A programmable automated valve controls the raffinate recovery.

The liquid feed can be supplied on two parts of the column, in the middle and at the top.

Characteristics of the column (other are possible):

- Column height : 2 m composed of 2 stages
- Diameter: 38 mm.
- Design pressure 300 bar
- Design temperature : 200°C.

High pressure pump :

- Volumetric piston pumps with jacketed head(s) for cooling. Our type of pumps has the best reliability and almost no maintenance and operation costs.
- CO_2 flow rate is controlled automatically with a frequency variator and a coriolis mass flowmeter that gives an indication of the flowrate of the fluid at the inlet of the extractor.
- Max Flow rate : 24 kg/h at 350 bar

Heat Exchangers :

- Condenser : The condenser allows to liquefy the gaseous CO_2 prior to recycling to the pump. It is cooled by a propylene glycol / water mixture supplied by the chiller.
- Heater: The heater allows to heat the CO_2 after the pump in a range of temperatures from 20 to 150° C.
- The column is heated by electrical jacket. Separex develop very precise controls for these heating to obtain a quick and precise temperature control.

Optionally, we propose to work at higher temperatures like 200 or 300°C.

Top And Bottom Ends:

Single screw cover lid at the bottom and at the top.

Bottom part design:

- Lower filtering plate to stop the column packing + homegenuous repartition of CO_2
- Lower section for liquid / gas phase separation
- 2 x sapphire windows for level visualisation

Drain at the bottom with automated valve in series with needle valve for smooth and automated raffinate collection

Top and intermediate part design

- Liquid distributors for liquid feed repartition
- Temperature measurement
- Free sampling port

Extract collection and exit to be sent to pressure control valve and separators placed on extractor skid.

The mixture leaving the column composed of extract/solvents/CO_2 is depressurised in a back pressure regulator and are then sent into a cyclonic separators (patented design) in which the extract or the solvents are separated from CO_2 that can be recycled. The enthalpy required for this separation is brought by heating the separators on is jacket.

The design and the capacity of each separator is computed for an optimal separation and the design will be adapted depending on the flow rate option that is chosen.

Installation Requirements

Turn key system installed on a skid on wheels to be connected to :

- Liquid CO_2 stored in cylinder
- Electricity 400 V 50 Hz
- Vent line 16 mm pipe to be connected outside

A chiller supplied by SEPAREX is connected very easily to the main skid. It can be placed next to the system or in another room.

Dimension : 1.5 m x 0.8 m x 2.5 m + chiller

Materials

High pressure, corrosion and chemical inertia requires stainless steel material. Stainless steel 316 L (1.4404) is usually used for most components. Equivalent corrosion resistant stainless steels with better mechanical properties are also used when required by the design, especially when working at high pressures and high temperatures.

The gaskets are either metallic, in P.T.F.E or compatible elastomers

Operation

The unit is controlled by an operator from a control box placed on the skid where controllers, pressure and temperature indicators are displayed. Control box allow all PID controls redundant interlocks, parameter setting and optional connection to PLC, PC, etc. Valves are mounted on the frame and are manually operated directly on the equipment. Temperature and pressure safety guaranties the safe operation at any time.

An option consists in adding a data acquisition module for operating parameters storage and possible exploitation on a PC.

Other automation options are also available and can be justified for remote operation. In this option a friendly PC based software is proposed and can propose

- Display of all parameters in a synoptic view of the process
- Process parameters choice and record
- Alarm parameters choice, detection and record
- Curve display of all parameters
- Storage of all process parameters on data files

Safety

This equipment will be designed and constructed in accordance with the European Union safety standard of machine construction (CE conformity declaration). EC rules and standards are used for pressure vessels and electrical devices. Other standards may be used if required.

The unit has several independent and redundant safety levels on all critical parameters. Control system always put the devices in a passive state in case of alarm or default detection.

The system is not designed to be used in Explosion proof environment unless specified. All connections are checked to avoid sparks.

All vessels are designed and manufactured according to European pressure equipment directive PED 97/23 EC. It is important to note that this type of equipment also require a global inspection of the assembly by a third party according to PED 97/23.

The high pressure pump has:

- An automatic switch- off system in case of over pressure;
- An internal safety valve by- passing the process fluid when the maximum pressure is reached.

Every capacity is provided with:

- A safety valve,
- A pressure indicator,
- A manual valve for fast draining.

Vent line:

All the draining points are connected to a main vent line whose diameter is designed to prevent plugging problems with the freezing of product or dry ice. It must be connected for outside release.

Heaters/Cooler:

Each heating bath has a high temperature safety system. The cooling bath has a low temperature safety system.

SEPAREX is always ready to help client during the construction to participate in all safety analysis, safety reviews for the installation and operation of this high pressure unit. We can advise for the implementation of safety procedures, for the operation of the system, for the

installation of the right type of instruments, detectors, use of personal protection, emergency procedures, etc.. All alarms and detectors placed in the environment and building are at client's charge.

Guarantees

- The supplier guarantees the right to use the supplied equipment and design concepts used for the plant construction and operation.
- The supplier guarantees the good operation of the plant during one year and shall change any defective part (excepted consumables and parts that ought to be changed normally).
- The supplier will do its best to study and realize the plant modifications required by the clients, at the client's charge.
- The supplier does not guarantee the right to use the plant in order to treat or elaborate products if such operations are covered by patents owned by third persons or companies.
- SEPAREX guarantee to be able to replace any defective part for a period of at least 10 years.
- SEPAREX can propose services like extensions of guarantee period, preventive maintenance contracts, holding of spare parts available within 24 hours.

Maintenance:

In order to ease preventive and curative maintenance operations and to guarantee equipment robustness and reliability, the followings elements are taken into account :

- Ease of access and dismounting. From the mechanical design of the components, 3 D drawing arrangement to design qualification, access and components reliability are taken into account. These points are systematically reviewed with the client and a continuous improvement methodology is applied with the valuable feedback from the operators of our systems.
- The training offered during equipment start- up shall allow the operators to be independent on the main maintenance operations.
- Preventive maintenance protocols and curative maintenance instructions are detailed in the documentation supplied with the equipment. SEPAREX also gives a list of necessary spares parts that are usually maintained in stock in our site. SEPAREX proposes maintenance contracts that covers a periodic review of operation and safety devices (instrumentation calibration, advice and review on the safety systems, proposition of modifications).

Price And Delivery Schedule Proposal

Prices :

SFF 2m : 90 000 EUROS. Delivered DDU France or CIF European Airport

Options :

- Liquid feed pump (HPLC pump for example): to be discussed depending on needs
- PC and datalogger
- Datalogger exporting files on PC for pressure and temperature conditions in extraction and separation section : + 6000 Euros

A.7 Flavex Aromats India Ltd.

Flavex India has a primary focus of solid extraction pilot plants, but still opted to provide a quote after being approached. Hence they could not provide a photo or a flow diagram, but the process description is of some relative value. The following process description and details was received from Flavex with the quote and typed over as is:

Introduction

The system offered consists of one set of liquid feed extractor with continuous feed of liquid material along with retention of the unextracted liquid, designed to operate at max 300 bar, 135°C & provided with suitable CO_2 circulation pump., 1 no separator operating at a max pressure of 60 bar, 30°C. There will be no reflux arrangement at the column top.

Scope of Supply

The SCFE plant package consisting of following items.

1. Extractor 40 mm id, 4m height, jacketed for circulation of hot oil, made of SS 304. Designed for 300 Bar, 135 0C with a 5 lit bottom receiver non jacketed to receive the bottoms unextracted matter, a separator to knock out the bulk liquid entrained with the gas at the top (this is not designed for flooding scenario). .
2. Product separator 1 lit. capacity made of SS 304, provided with jacket or for heating Designed for 66 bar 60°C.
3. Set of 4 heat exchangers consisting of 4 heat exchangers of which 2 number exchangers for CO_2 condensing, pre- cooling, are designed for 70 Bar at 60 Deg C while 2 others for preheating to 135° C & are designed for 330 Bar at 135° C made of SS 304. MOC all SS304.
4. CO_2 circulation pump air operated arrangement to vary the capacity & made of SS 304 high pressure CO2 contact parts while rest is in carbon steel with max pressure 350 Bar at 15 deg C CO_2 flow 55 Lit/hr. The compressed air will be from electrically driven air compressor mounted on a receiver. (we reserve right to change the drive from air operated to electrical operated).
5. Back pressure regulator:- of suitable size, Designed for 350 Bar, reduction to 60 bar.
6. CO_2 holding tank (about 15 lit) provided with cooling arrangement & made of SS 304 & provided with jacket or limpet coil for cooling. Designed for 66 Bar, 50° C (CO_2 side) & 6 Bar on utility side.
7. Liquid feed system :- Incorporating a 5 lit measure vessel, a plunger pump to vary the feed flow rate in the range of about 3 lph to 10 lph based on water properties, feed line entering the extractor at the top section just below a separator. All material will be SS304/316 combination.

8. Chilling unit of suitable capacity with circulation pump of suitable capacity fully automated for unattended operation.
9. Hot oil heating unit of about 18 KW capacity with circulation pump automated for unattended operation.
10. Instrumentation:- PLC based panel mounted temperature, pressure indicators, flow indicators operation interlocks for safety purpose etc.
11. Control panel for operation of both the utilities in unattended manner.
12. Skid to mount the equipment set up. One each separate for the modules or one bigger common to accommodate both the modules. All in carbon steel coated suitably.
13. Valves, piping fittings on process side in SS304:- all CO_2 side high pressure piping will be to with stand 350 bar g & low CO_2 pressure circuit will be to withstand 100 bar pressure.
14. Valves piping fittings for hot oil, chilled water package unit to respective process equipment & hot oil pump to respective process equipment, in CS/GI etc.

Price / Charges

The price for the scope stated above is USD 115000 (US Dollar one hundred & fifteen thousand) FOB Mumbai port of India.

Warrantee

One year from the date of supply against manufacturing defects, for items manufactured by us. This is subject to the condition that "FLAVEX is satisfied fully about the use of standard procedures of installation, operation and maintenance given by FLAVEX are followed rigorously'. The wearing components durables like gaskets, tube oils, electrical components etc. are excluded from this. The warrantee period is 12 months from the date of demonstration of the trial at our factory for the manufacturing defects.*

Appendix B: Safety and Certification Forms

The Material Safety Data Sheet or MSDS forms for all the substances used in this study are gathered in this section. After that the departmental risk analysis form is available. The order of appearance is as follows:

B.1 MSDS for Dowtherm A

Material Safety Data Sheet

Section 1 - Product information

Product Identifier:	Dowtherm A	**Manufacturer/Supplier:**	Dow Chemical Company
Compound CAS no	8004-13-5	**Identified uses:**	Heat Transfer
Molecular Formula	$C_{24}H_{20}O$		Laboratory Chemicals

Section 2 Ingredients/Identity information

Component	CAS No	Percentage	Hazardous
Diphenyl oxide	1001-84-8	73%	Yes
Biphenyl, diphenyl	92-52-4	27%	Yes

Section 3 Physical/Chemical Characteristics

Physical State:	Liquid	**Molar Weight:**	165.89 g/mole
Odour:	Disagreeable characteristic odour	**Specific Gravity:**	1.060
		Melting range:	12-14°C
Taste:	Not available	**Boiling point:**	257°C
Colour:	Clear	**Vapour Pressure:**	0.025 mmHg at 25 °C
pH:	n/a		
Solubility in Water:	Not miscible		

Section 4 Fire and Explosion Hazard Data

Flammability of the Product:	Combustible at high temperature or in presence of sparks or open flames
Auto-Ignition Temperature:	599°C
Flash point:	Closed Cup: 113°C
Flammable Limits:	VAPOUR: lower: 0.8%; upper: 7.0%
Extinguishing Media:	Use dry chemical powder, spray, fog, foam or CO_2 as the situation demands
Explosion Hazards	n/a

Section 5 Reactivity Data

Stability:	Product is stable.
Instability Temperature	Not Available
Conditions of Instability:	Incompatible materials (strong oxidisers), high heat.
Substance incompatibility:	Reactive with strong acids, bases or oxidizing agents
Corrosivity:	Non Corrosive
Special remarks	None

Continues on next page...

(MSDS B.1 Dowtherm, continues)

Section 6 Health Hazard Data
Potential Acute Health Effects:
Causes irritation in case of skin contact (permeator), eye contact, or ingestion. Inhalation can cause nausea and headaches.
Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Contains component(s) which have caused cancer in laboratory animals. However, biphenyl is not genotoxic, and the relevance of cancer to humans is unknown. MUTAGENIC EFFECTS: Not known or anticipated. TERATOGENIC EFFECTS: Contains component(s) which, in laboratory animals, have been toxic to the fetus only at doses toxic to the mother. Repeated or prolonged exposure may cause Gastrointestinal disturbance, Dermatitis, To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.
Toxicological Information:
Draize test, rabbit, eye: 500 mg/24H Mild
Draize test, rabbit, skin: 500 mg/24H Mild;
Oral, mouse: LD50 = 3200 mg/kg;
Oral, rabbit: LD50 = 4200 mg/kg;
Oral, rat: LD50 = 2460 mg/kg;

Section 7 First Aid Measures
Eye Contact:
Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention if irritation occurs and persists.
Skin Contact:
Wash with soap and water. Cover the affected skin with an emollient. Get medical attention if irritation develops. Cold water may be used.
Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.
Ingestion:
Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If large quantities of this material are swallowed, call a physician immediately. Loosen tight clothing such as a collar, tie, belt or waistband.

Section 8 Precautions for Safe Handling and Use
Handling:
Wash thoroughly after handling. Remove contaminated clothing and wash before reuse. Avoid contact with eyes, skin, and clothing. Keep container tightly closed. Avoid ingestion and inhalation. Use with adequate ventilation.
Storage
Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Containers of this material may be hazardous when empty since they retain product residues (dust, solids, vapours, liquid); observe all warnings and precautions listed for the product.

Section 9 Accidental Release Measures
Absorb spill with inert material (e.g. vermiculite, sand or earth), then place in suitable container. Avoid runoff into storm sewers and ditches which lead to waterways. Clean up spills immediately, observing precautions in the Protective Equipment section. Remove all sources of ignition. Provide ventilation.

B.2 MSDS for CO_2

Material Safety Data Sheet

Section 1 - Product information

Product Identifier:	CO_2	**Manufacturer/Supplier:**	Merck Chemicals
Synonyms:	Carbon dioxide	**Identified uses:**	Laboratory chemicals
Chemical Formula:	CO_2		Chemical Intermediates

Section 2 Ingredients/Identity information

Component	CAS No	Percentage	Hazardous
Carbon Dioxide	124-38-9	99.9%	No

Section 3 Physical/Chemical Characteristics

Physical State:	Gas/Liquid	**Molar Weight:**	44.011 g/mole
Odour:	Odourless	**Specific Gravity:**	1.977×10^{-3}
Taste:	Not available	**Sublimation Temp:**	-79°C
Colour:	Colourless	**Vapour Pressure:**	n/a
pH:	n/a		
Solubility in Water:	Soluble		

Section 4 Fire and Explosion Hazard Data

Flammability of the Product:	n/a
Auto-Ignition Temperature:	n/a
Flash point:	n/a
Flammable Limits:	n/a
Extinguishing Media:	n/a
Explosion Hazards	Passing carbon dioxide over a mixture of sodium peroxide and aluminium or magnesium may explode.

Section 5 Reactivity Data

Stability:	Product is stable.
Instability Temperature	Not Available
Conditions of Instability:	Incompatible materials.
Substance incompatibility:	Certain reactive metals, hydrides, moist caesium monoxide
Corrosivity:	Non Corrosive
Special remarks	None

Continues on next page...

(MSDS B.2 CO_2, continues)

Section 6 Health Hazard Data
Potential Acute Health Effects:
Carbon dioxide is the most powerful cerebral vasodilator known. Inhaling large concentrations causes rapid circulatory insufficiency leading to coma and death.
Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Not known or anticipated. MUTAGENIC EFFECTS: Not known or anticipated. TERATOGENIC EFFECTS: Exposure of female rats to 60,000 ppm carbon dioxide for 24 hours has produced toxic effects to the embryo and fetus in pregnant rats. Toxic effects to the reproductive system have been observed in other mammalian species at similar concentrations. Repeated or prolonged exposure is not known to aggravate medical condition.
Toxicological Information:
LC50 Rat Inhalation - 470 000 ppm with an 30 min exposure time

Section 7 First Aid Measures
Eye Contact:
Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention if irritation occurs.
Skin Contact:
Wash with soap and water. Cover the affected skin with an emollient. Get medical attention if irritation develops. Cold water may be used.
Frostbite
Try to warm up the frozen tissues and seek medical attention.
Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.
Ingestion:
n/a

Section 8 Precautions for Safe Handling and Use
Handling:
Wash thoroughly after handling. Do not puncture or incinerate container. Use equipment rated for cylinder pressure. Close valve after each use and when empty. Protect cylinders from physical damage; do not drag, roll, slide, or drop. Avoid contact with eyes, skin, and clothing. Prevent entrapment of liquid in closed systems or piping without pressure relief devices. Keep container tightly closed. Avoid inhalation. Use with adequate ventilation.
Storage
Cylinders should be stored upright, with valve protection cap in place, and firmly secured to prevent falling or being knocked over. Cylinder temperatures should not exceed 52 °C.

Section 9 Accidental Release Measures
Immediately contact emergency personnel. Keep unnecessary personnel away. Use suitable protective equipment. Shut off gas supply if this can be done safely. Isolate area until gas has dispersed.

B.3 MSDS for PEG 400

Material Safety Data Sheet

Section 1 - Product information

Product Identifier:	PEG 400	**Manufacturer/Supplier:**	Merck Chemicals
Synonyms:	Polyethylene glycol (PEG)	**Identified uses:**	Laboratory chemicals
	polyethylene oxide (PEO)		Chemical Intermediates
	polyoxyethylene (POE)		Food Processing & Packaging
	Poly(oxy-1,2-ethanediyl)		
Chemical Formula:	$H(OCH_2CH_2)nOH$		Pharmaceuticals

Section 2 Ingredients/Identity information

Component	CAS No	Percentage	Hazardous
Polyethylene glycol 400	25322-68-3	100%	No

Section 3 Physical/Chemical Characteristics

Physical State:	Liquid	**Molar Weight:**	400 (374-432) g/mole
Odour:	Odourless	**Specific Gravity:**	1.1254
Taste:	Not available	**Melting range:**	4-8°C
Colour:	Clear	**Boiling point:**	Not available
pH:	n/a	**Vapour Pressure:**	< 0,01 hPa at 20 °C
Solubility in Water:	Complete		

Section 4 Fire and Explosion Hazard Data

Flammability of the Product:	Combustible at high temperature or in presence of sparks or open flames	
Auto-Ignition Temperature:	Not available	
Flash point:	Closed Cup: 226.67°C	Open Cup: 231.11°C
Flammable Limits:	Not available	
Extinguishing Media:	SMALL FIRE: Use DRY chemical powder.	
	LARGE FIRE: Use water spray, fog or foam.	
Explosion Hazards	n/a	

Section 5 Reactivity Data

Stability:	Product is stable.
Instability Temperature	Not Available
Conditions of Instability:	Incompatible materials (strong oxidisers), high heat.
Substance incompatibility:	Reactive with oxidising agents, acids, alkalis
Corrosivity:	Non Corrosive
Special remarks	Hydrophilic, Hygroscopic

Continues on next page...

(MSDS B.3 PEG 400, continues)

Section 6 Health Hazard Data
Potential Acute Health Effects:
Slightly hazardous in case of skin contact (irritant, permeator), eye contact (irritant), ingestion or inhalation.
Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Not known or anticipated. MUTAGENIC EFFECTS: Not known or anticipated. TERATOGENIC EFFECTS: Not available. Repeated or prolonged exposure is not known to aggravate any medical condition.
Toxicological Information:
Oral Rat LD50 - 30.2 g/kg

Section 7 First Aid Measures
Eye Contact:
Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention if irritation occurs.
Skin Contact:
Wash with soap and water. Cover the affected skin with an emollient. Get medical attention if irritation develops. Cold water may be used.
Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.
Ingestion:
Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If large quantities of this material are swallowed, call a physician immediately. Loosen tight clothing such as a collar, tie, belt or waistband.

Section 8 Precautions for Safe Handling and Use
Handling:
Wash thoroughly after handling. Remove contaminated clothing and wash before reuse. Avoid contact with eyes, skin, and clothing. Keep container tightly closed. Avoid ingestion and inhalation. Use with adequate ventilation.
Storage
Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Containers of this material may be hazardous when empty since they retain product residues (dust, solids, vapours, liquid); observe all warnings and precautions listed for the product.

Section 9 Accidental Release Measures
Small Spill:
Dilute with water and mop up, or absorb with an inert dry material and place in an appropriate waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.
Large Spill:
Absorb with an inert material and put the spilled material in an appropriate waste disposal. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system.

B.4 Pressure Test Certificates and Vessel Certification

The following 6 pages contain, in order, the pressure testing and recertification certificates of the three high pressure vessels, being the:

- Solvent buffer tank V 2- 1
- Large diameter column C 3- 2
- Separator vessel V 4- 1.

RITC (Pty) Ltd

57 Williams Way, Racing Park
Table View
Tel: 021 556 4884
Fax: 086 694 2419

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LVUP062

DECLARATION OF CONFORMITY

CLIENT: University of Stellenbosch –Process Engineering

EQUIPMENT TYPE: Solvent Gas Tank

DESIGN VERIFICATION STANDARD: ASME VIII DIV 1 2013

DESIGN ENGINEERS: SCHREUDER ENGINEERING SERVICES

DESIGN CALCULATION REF: DD740.1015

VESSEL DATA:

Vessel serial no:	740.1015
Country of origin:	Germany
Manufacturer:	SITEC
Year of Manufacture:	1991
Re- Certified to:	RSA/CI/OHSA 8.1 2013
Design pressure:	7432kPa
Design Temperature:	0°C Min – 50°C Max
Capacity:	0.010M ^{3}
Corrosion Allowance	Nil
MOC	SA - 240 Gr 316L / SA – 312 TP 316
SANS 347 Hazard Category:	III

Declaration of Conformity: We hereby declare that the vessel as described above, which we have inspected, tested and re-certified is suitable for the purpose for which it is intended and meets the design requirements of the design code stated above. We further declare that the vessel complies with the requirements of the OHS Act Pressure Equipment Regulations 2009 and SANS 347: 2012 Edition 2.

TECHNICAL SIGNATORY:

RITC (Pty) Ltd: A.Stoltz

Date: 28/03/2014

Report No. DOC/21706-02

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LVUP062

RITC (Pty) Ltd

PRESSURE VESSEL INSPECTION REPORT, TEST CERTIFICATE & CERTIFICATE OF CONTINUANCE

Client: University of Stellenbosch
Process Engineering

Report No: RN 21706-02

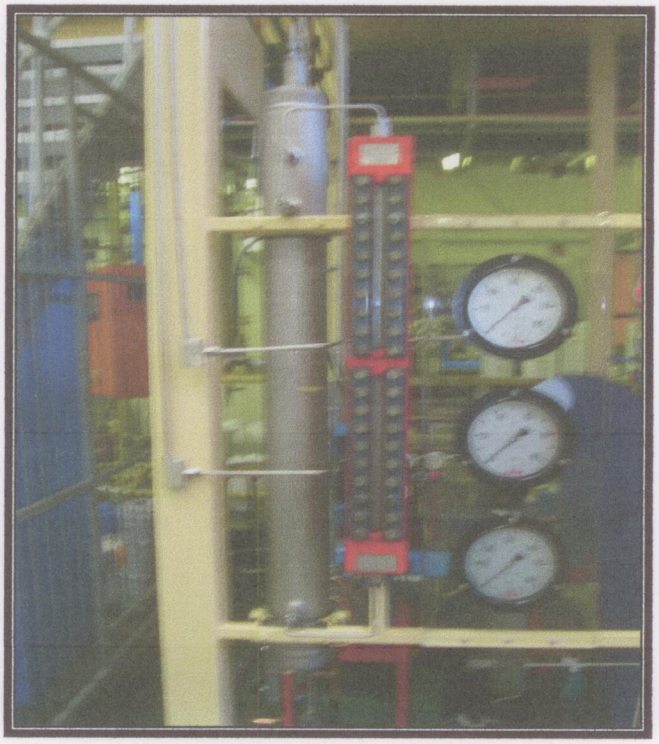

Figure 1:Solvent Gas Tank 740.1015

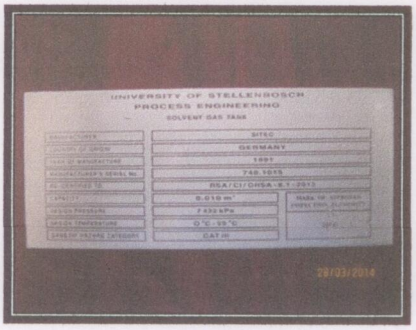

Figure 2: New Data Plate

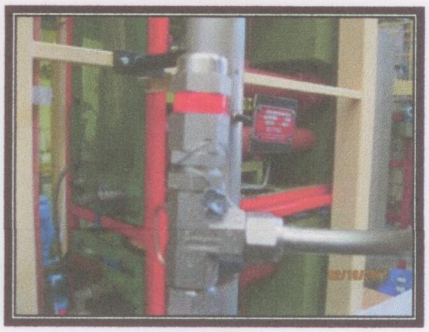

Figure 3: Safety Relief Valve

Compiled by: A.Stoltz
Date of Inspection: 02 October 2013

Any holder of this document is advised that information contained hereon reflects the Company's findings at the time of its intervention only and within the limits of Client's instructions, if any. The Inspection undertaken by RITC on behalf of the Client does not relieve the owner of his responsibilities under Statutory Regulations.

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RITC (Pty) Ltd

PRESSURE VESSEL INSPECTION REPORT, TEST CERTIFICATE & CERTIFICATE OF CONTINUANCE

Client : University of Stellenbosch

Report No: 21706-01

Type of Pressure Vessel:	Solvent Gas Tank	Code of Construction:	Re-Certified to RSA/CI/OHSA 8.1 13
Manufacturers Serial No:	740.1015	Manufacturer:	SITEC
Year of Manufacture:	1991	Design Pressure:	7432kPa
Capacity:	0.010 m³	Design Temperature:	0°C - 50°C
Operating Medium:	Liquefied Solvent Gas	Date of Inspection:	02/10/2013

Inspection Report:

Internal: No access to internal surface of vessel.

External: Shell and heads smooth and in good condition. End cap to shell welds all smooth and of even profile. All nozzles and supports in good condition.

Safety valve: PSV verified, the user shall ensure that the safety valve is set at or below the re-certified design pressure of 7432kPa and locked at this position.
Pressure Gauge: The user shall ensure that at least one pressure measuring device with a range of 0-15000kPa be fitted to the vessel.

Recommendations: The internal surface of the vessel must be inspected by means of remote endoscopic method during the next statutory intervention.

Pressure Test: (Test pressure as per the requirements of the OHSA P.E.R.)

Range of pressure gauge:	0 - 50000kPa	Test medium:	Water
Gauge Serial no:	P938-8	Test pressure:	9300kPa
Gauge calibrated:	23/05/2013	Pressure held for:	30 Min

Pressure well held during hydrostatic pressure test with no leaks or anomalies noted.

A.Stoltz (CP 'PV' 602) Date: 02/10/2013

Certificate of Continuance:
The Solvent Gas Tank is considered fit for service and in compliance with the minimum requirements of the OHSA Pressure Equipment Regulations 2009. Inspection frequency: 36 months. Next inspection is due by **02 October 2016.**

Signed: _____ Name: A.Stoltz Date: 28/03/2014

IPE 518 CPPV 602

RITC (Pty) Ltd

57 Williams Way, Racing Park
Table View
Tel: 021 556 4884
Fax: 086 694 2419

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LVUP 062

DECLARATION OF CONFORMITY

CLIENT: University of Stellenbosch –Process Engineering

EQUIPMENT TYPE: Column

DESIGN VERIFICATION STANDARD: ASME VIII DIV 1/2 2013

DESIGN ENGINEERS: SCHREUDER ENGINEERING SERVICES

DESIGN CALCULATION REF: DD740.1056

VESSEL DATA:

Vessel serial no:	740.1056
Country of origin:	Germany
Manufacturer:	SITEC
Year of Manufacture:	1990
Re- Certified to:	RSA/CI/OHSA 8.1/2 2013
Design pressure:	32424kPa
Design Temperature:	0°C Min – 200°C Max
Capacity:	0.002M ^{3}
Corrosion Allowance	Nil
MOC	SA 240 Gr 316Ti / SA 193 Gr B8M stainless steel
SANS 347 Hazard Category:	III

Declaration of Conformity: We hereby declare that the vessel as described above, which we have inspected, tested and re-certified is suitable for the purpose for which it is intended and meets the design requirements of the design code stated above. We further declare that the vessel complies with the requirements of the OHS Act Pressure Equipment Regulations 2009 and SANS 347: 2012 Edition 2.

TECHNICAL SIGNATORY:

RITC (Pty) Ltd: A.Stoltz

Date: 28/03/2014

sanas Inspection Body
LVUP062

RITC (Pty) Ltd

PRESSURE VESSEL INSPECTION REPORT, TEST CERTIFICATE & CERTIFICATE OF CONTINUANCE

Client: University of Stellenbosch
Process Engineering

Report No: RN 21706-01

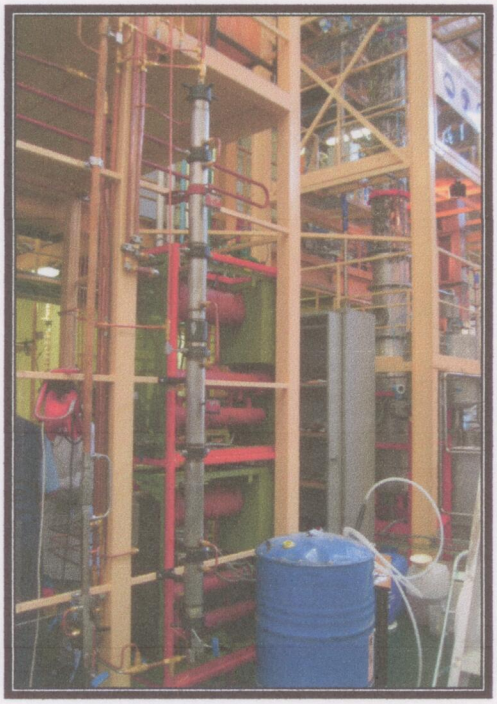

Figure 1:Column 740.1056

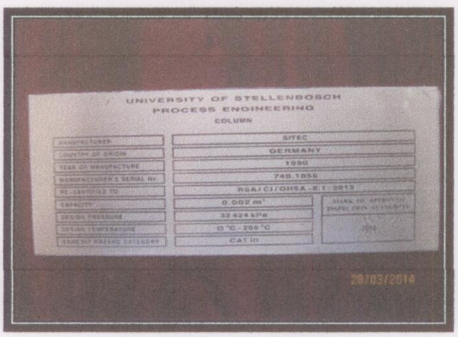

Figure 2: New Data Plate

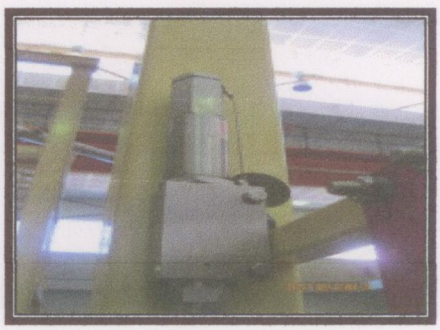

Figure 3: Safety Relief Valve

Compiled by: A.Stoltz
Date of Inspection: 02 October 2013

A.Stoltz IPE 518 CPPV 602 RITC (Pty) Ltd

Any holder of this document is advised that information contained hereon reflects the Company's findings at the time of its intervention only and within the limits of Client's instructions, if any. The Inspection undertaken by RITC on behalf of the Client does not relieve the owner of his responsibilities under Statutory Regulations.

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RITC (Pty) Ltd

PRESSURE VESSEL INSPECTION REPORT, TEST CERTIFICATE & CERTIFICATE OF CONTINUANCE

Client : University of Stellenbosch

Report No: 21706-01

Type of Pressure Vessel:	Column	Code of Construction:	Re-Certified to RSA/CI/OHSA 8.1/2 13
Manufacturers Serial No:	740.1056	Manufacturer:	SITEC
Year of Manufacture:	1990	Design Pressure:	32 424kPa
Capacity:	0.002 m³	Design Temperature:	0°C - 200°C
Operating Medium:	Liquid Organics/ Solvent Gas	Date of Inspection:	02/10/2013

Inspection Report:

Internal: No access to internal surface of vessel.

External: Shell and ends smooth and in good condition. Threads and end caps all visually sound with no degradation evident. All nozzles and supports in good condition.

Safety valve: PSV verified, the user shall ensure that the safety valve is set at or below the re-certified design pressure of 32 424kPa and locked at this position.
Pressure Gauge: The user shall ensure that at least one pressure measuring device with a range of 0-60000kPa be fitted to the vessel.

Recommendations: It is recommended that all nozzle to jacket and jacket to vessel shell welds be pickled and passivated. The internal surface of the vessel must be inspected by means of remote endoscopic method during the next statutory intervention.

Note: The vessel jacket with a volume of 0.001m³ and a design pressure of 810kPa is categorized as "SEP" as per SANS 347 2012 Ed 2 and as such is not regulated under the OHS Act PER.

Pressure Test: (Test pressure as per the requirements of the OHSA P.E.R.)

Range of pressure gauge:	0 - 50000kPa	Test medium:	Water
Gauge Serial no:	P938-8	Test pressure:	40530kPa
Gauge calibrated:	23/05/2013	Pressure held for:	30 Min

Pressure well held during hydrostatic pressure test with no leaks or anomalies noted.

A.Stoltz (CP 'PV' 602) Date: 02/10/2013

Certificate of Continuance:
The Column is considered fit for further service and in compliance with the minimum requirements of the OHSA Pressure Equipment Regulations 2009. Inspection frequency: 36 months. Next inspection is due by **02 October 2016.**

Signed: _____ Name: A.Stoltz Date: 28/03/2014

RITC (Pty) Ltd

57 Williams Way, Racing Park
Table View
Tel: 021 556 4884
Fax: 086 694 2419

sanas Inspection Body
LVUP062

DECLARATION OF CONFORMITY

CLIENT: University of Stellenbosch –Process Engineering

EQUIPMENT TYPE: Separator

DESIGN VERIFICATION STANDARD: ASME VIII DIV 1 2013

DESIGN ENGINEERS: SCHREUDER ENGINEERING SERVICES

DESIGN CALCULATION REF: DD740.1068

VESSEL DATA:

Vessel serial no:	740.1068
Country of origin:	Germany
Manufacturer:	SITEC
Year of Manufacture:	1991
Re- Certified to:	RSA/CI/OHSA 8.1 2013
Design pressure:	10133kPa
Design Temperature:	0°C Min – 200°C Max
Capacity:	0.011M ^{3}
Corrosion Allowance	Nil
MOC	SA - 240 Gr 316Ti
SANS 347 Hazard Category:	IV

Declaration of Conformity: We hereby declare that the vessel as described above, which we have inspected, tested and re-certified is suitable for the purpose for which it is intended and meets the design requirements of the design code stated above. We further declare that the vessel complies with the requirements of the OHS Act Pressure Equipment Regulations 2009 and SANS 347: 2012 Edition 2.

TECHNICAL SIGNATORY:

RITC (Pty) Ltd: A.Stoltz **Date: 28/03/2014**

sanas Inspection Body
LVUP062

RITC (Pty) Ltd

PRESSURE VESSEL INSPECTION REPORT, TEST CERTIFICATE & CERTIFICATE OF CONTINUANCE

Client: University of Stellenbosch
Process Engineering

Report No: RN 21706-03

Figure 1: Separator 740.1068

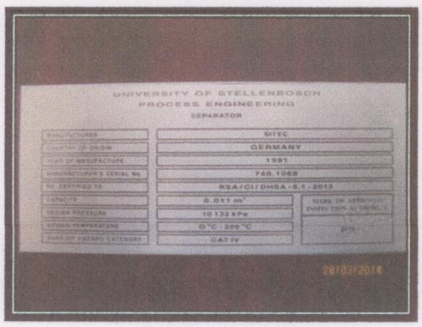


Figure 2: New Data Plate

Figure 3: Safety Relief Valve

Compiled by: A.Stoltz
Date of Inspection: 02 October 2013

A.Stoltz
PrEng 518
CPPV 602
RITC (Pty) Ltd

sanas Inspection Body
LVUP062

RITC (Pty) Ltd

PRESSURE VESSEL INSPECTION REPORT, TEST CERTIFICATE & CERTIFICATE OF CONTINUANCE

Client : University of Stellenbosch

Report No: 21706-03

Type of Pressure Vessel:	Separator	Code of Construction:	Re-Certified to RSA/CI/OHSA 8.1 13
Manufacturers Serial No:	740.1068	Manufacturer:	SITEC
Year of Manufacture:	1991	Design Pressure:	10133kPa
Capacity:	0.011 m³	Design Temperature:	0°C - 200°C
Operating Medium:	Liquid Organics/Solvent Gas	Date of Inspection:	02/10/2013

Inspection Report:

Internal: Top lid removed for internal inspection. Entire internal surface smooth and in good condition with no anomalies noted. Top lid threads and vessel threads appear visually sound.
External: Shell and ends noted to be smooth and in good condition. Jacket to vessel shell welds smooth and of even profile. All nozzles appear visually sound.

Safety valve: PSV verified, the user shall ensure that the safety valve is set at or below the re-certified design pressure of 10133kPa and locked at this position.
Pressure Gauge: The user shall ensure that at least one pressure measuring device with a range of 0-20000kPa be fitted to the vessel.

Note: The vessel jacket with a volume of 0.001m³ and a design pressure of 506kPa is categorized as "SEP" as per SANS 347 2012 Ed 2 and as such is not regulated under the OHS Act PER.

Pressure Test: (Test pressure as per the requirements of the OHSA P.E.R.)

Range of pressure gauge:	0 - 50000kPa	Test medium:	Water
Gauge Serial no:	P938-8	Test pressure:	12666kPa
Gauge calibrated:	23/05/2013	Pressure held for:	30 Min

Pressure well held during hydrostatic pressure test with no leaks or anomalies noted.

A.Stoltz (CP 'PV' 602) Date: 02/10/2013

Certificate of Continuance:
The Separator is considered fit for service and in compliance with the minimum requirements of the OHSA Pressure Equipment Regulations 2009. Inspection frequency: 36 months. Next inspection is due by **02 October 2016.**

Signed: Name: A.Stoltz Date: 28/03/2014

Appendix C: Sensor Placement, Calibrations, Alarm interlocks and Commissioning

In this section all the placement of each sensor is listed, followed by sensor calibration procedures and calibration curves for the liquid feed pumps. Next, the testing of the automation sequences, alarms and safety interlocks on the HMI are discussed. Finally the Commissioning procedure of the pilot plant is discussed.

C.1 Sensor Placement

In this section brief description of the function and rationale of each sensor in the pilot plant is given. All subsequent referrals to equipment numbers will refer to the equipment as identified in the P&IDs in Section 4.2.

Temperature Sensors

Sensor	Description (Measures the temperature of; Monitoring ensures)
TE 1-1	Liquid feed to the pumps. Ensures the correct liquid temperature going into the liquid pumps. This avoids blockages, especially for solid or highly viscous feeds.
TE 2-1	Liquid solvent to the solvent pump. Ensures liquid feed to the solvent pump for proper pumping.
TE 3-1	Supercritical solvent to the columns. Ensures the solvent enters the columns at the correct temperature and in the supercritical phase.
TE 3-2	Inside temperature of column C3-2 top region. Reports process temperature for correct experimental conditions.
TE 3-3	Surface temperature of column C3-2 top region. Indicates jacket temperature. Can be compared with TE 3-2 to determine heat transfer issues.
TE 4-1	Columns' top product before expansion. Ensures the correct temperature to avoid precipitation of the dissolved product.
TE 4-2	Separator V 4-1 temperature. Ensures correct separator temperature.

Pressure Gauges and Sensors

Sensor	Description (Measures the pressure of; Monitoring ensures)
PE 1-1	Liquid feed pressure from pumps to column. Ensures correct liquid feed pressure and lack of blockages.
PE 2-1	Solvent buffer tank pressure. Ensures correct solvent pressure and lack of blockages.
PE 3-1	Supercritical solvent feed to column. Ensures correct solvent feed pressure and lack of blockages.

Sensor	Description (Measures the pressure of; Monitoring ensures)
PE 4-1	Columns' top product before expansion. Physical failsafe for PIC 4-1 to ensure correct column pressure.
PE 4-2	Separator pressure. Physical failsafe for PIC 4-2 to ensure correct separator pressure.
PIC 4-1	Columns' top product before expansion. Used to control the columns' pressure in conjunction with control valve CV 4-1.
PIC 4-2	Separator V 4-1 pressure. Ensures correct separator pressure for product precipitation.

Level Indicators

Sensor	Description (Measures the level of; Monitoring ensures)
LE 2-1	Top liquid solvent level in solvent buffer tank V 2-1. Wards against overfilling the solvent circuit.
LE 2-2	Bottom liquid solvent level in solvent buffer tank V 2-1. Ensures a liquid feed to solvent pump P 2-1.
LE 2-3	Liquid level over the entirety of solvent buffer tank V 2-1. Used to monitor the amount of solvent in the system.
LE 3-1	Column C 3-2 bottom liquid level. Provides warning in the case of the column bottoms section filling up.
LE 3-2	Column C 3-2 top liquid level. Is used to monitor column flooding.
LE 4-1	Separator V 4-1 liquid level. Warns in the case of the separator becoming full.

C.2 Sensor calibrations

All the sensors were calibrated to ensure accurate measurement. The procedure followed for each sensor subtype is discussed below. The relevant HMI GUI calibration sheets can be seen in Figure C- 1 and Figure C- 2.

C.2.1 Temperature Sensors

All the temperature sensors are J type thermocouples. Thermocouples consist of a join of two dissimilar metals that produce a voltage due to electric potential. The voltage generated is dependent on the temperature of the join and can be tabulated as a reference in order to use them to tell temperature, as can be seen in Table C- 1 on the following page. J type thermocouples are composed of a positive iron leg and a negative constantan leg (45 % nickel-55% copper) and is advised for temperatures between -40°C and 750°C with a reported accuracy of ±1.5°C.

In order to calibrate the thermocouples a high accuracy temperature probe is submerged in hot water with the thermocouple. An offset value is then inserted into the HMI unit until the displayed value matches that of the high accuracy probe. The calibration is then tested by once again submerging both the thermocouple and the high accuracy probe into cold water and comparing the values.

C.2.2 Pressure Sensors and Gauges.

The pressure sensors were calibrated using known pressures, applied during pressure testing. As with the temperature sensors an offset value is inserted into the HMI for each sensor.

The readings on the pressure gauges were compared with the known pressures. All the gauges used were found to give good readings.

Table C- 1: Temperature-voltage reference table for J type thermocouples.

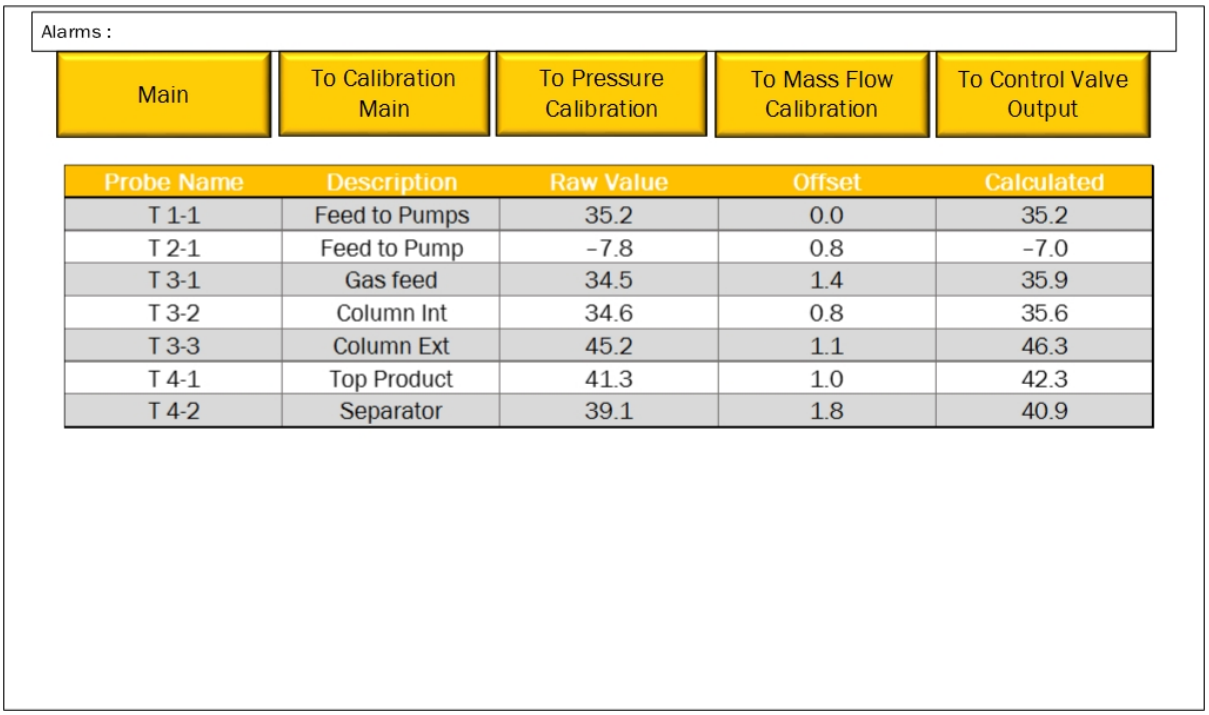
°C	0	1	2	3	4	5	6	7	8	9
-40	-1.961	-2.008	-2.055	-2.103	-2.15	-2.197	-2.244	-2.291	-2.338	-2.385
-30	-1.482	-1.53	-1.578	-1.626	-1.674	-1.722	-1.77	-1.818	-1.865	-1.913
-20	-0.995	-1.044	-1.093	-1.142	-1.19	-1.239	-1.288	-1.336	-1.385	-1.433
-10	-0.501	-0.55	-0.6	-0.65	-0.699	-0.749	-0.798	-0.847	-0.896	-0.946
0	0	-0.05	-0.101	-0.151	-0.201	-0.251	-0.301	-0.351	-0.401	-0.451
0	0	0.05	0.101	0.151	0.202	0.253	0.303	0.354	0.405	0.456
10	0.507	0.558	0.609	0.66	0.711	0.762	0.814	0.865	0.916	0.968
20	1.019	1.071	1.122	1.174	1.226	1.277	1.329	1.381	1.433	1.485
30	1.537	1.589	1.641	1.693	1.745	1.797	1.849	1.902	1.954	2.006
40	2.059	2.111	2.164	2.216	2.269	2.322	2.374	2.427	2.48	2.532
50	2.585	2.638	2.691	2.744	2.797	2.85	2.903	2.956	3.009	3.062
60	3.116	3.169	3.222	3.275	3.329	3.382	3.436	3.489	3.543	3.596
70	3.65	3.703	3.757	3.81	3.864	3.918	3.971	4.025	4.079	4.133
80	4.187	4.24	4.294	4.348	4.402	4.456	4.51	4.564	4.618	4.672
90	4.726	4.781	4.835	4.889	4.943	4.997	5.052	5.106	5.16	5.215
100	5.269	5.323	5.378	5.432	5.487	5.541	5.595	5.65	5.705	5.759
110	5.814	5.868	5.923	5.977	6.032	6.087	6.141	6.196	6.251	6.306
120	6.36	6.415	6.47	6.525	6.579	6.634	6.689	6.744	6.799	6.854
130	6.909	6.964	7.019	7.074	7.129	7.184	7.239	7.294	7.349	7.404
140	7.459	7.514	7.569	7.624	7.679	7.734	7.789	7.844	7.9	7.955
150	8.01	8.065	8.12	8.175	8.231	8.286	8.341	8.396	8.452	8.507
160	8.562	8.618	8.673	8.728	8.783	8.839	8.894	8.949	9.005	9.06
170	9.115	9.171	9.226	9.282	9.337	9.392	9.448	9.503	9.559	9.614
180	9.669	9.725	9.78	9.836	9.891	9.947	10.002	10.057	10.113	10.168
190	10.224	10.279	10.335	10.39	10.446	10.501	10.557	10.612	10.668	10.723
200	10.779	10.834	10.89	10.945	11.001	11.056	11.112	11.167	11.223	11.278
210	11.334	11.389	11.445	11.501	11.556	11.612	11.667	11.723	11.778	11.834

C.2.3 DP Cell

The DP cell has an on-line digital unit that is used to zero the sensor output. The DP cell is calibrated before experimentation at a certain pressure and temperature. This eliminates the effect of gravity on the elevated density of the CO_2 phase. This means that any pressure difference generated is only due to flow, and not the effects of gravity.

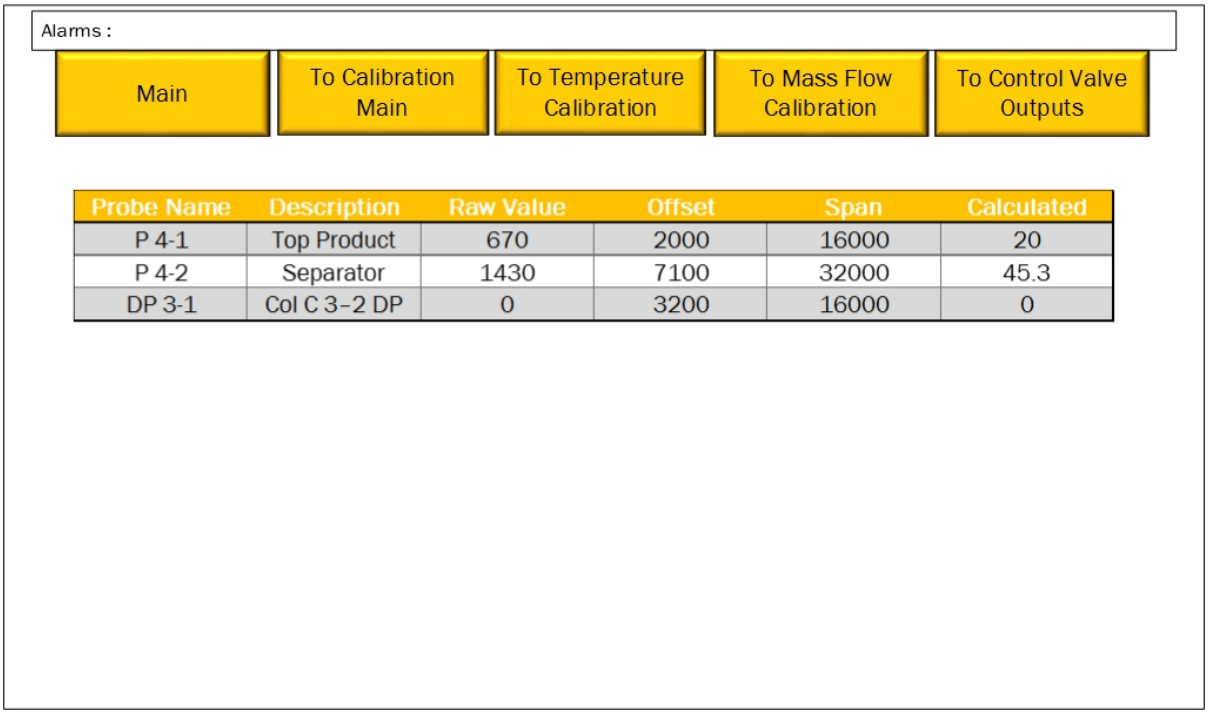
To calibrate the DP cell at a pressure and temperature state the column is operated at the required settings for about 5-10 minutes. This ensures that it is full of CO_2 at the correct temperature and pressure. Flow to the column is then turned off and the fluid in the column is allowed to settle. The DP cell reading is then monitored until a constant reading is displayed, after which it is zeroed on the sensor. Note that this procedure is only applicable to a specific pressure and temperature state and has to be recalibrated or a correction factor applied to the data afterward for use at a different state.

C.2.4 Typical Sensor Calibration Values and GUI



Probe Name	Description	Raw Value	Offset	Calculated
T 1-1	Feed to Pumps	35.2	0.0	35.2
T 2-1	Feed to Pump	-7.8	0.8	-7.0
T 3-1	Gas feed	34.5	1.4	35.9
T 3-2	Column Int	34.6	0.8	35.6
T 3-3	Column Ext	45.2	1.1	46.3
T 4-1	Top Product	41.3	1.0	42.3
T 4-2	Separator	39.1	1.8	40.9

Figure C- 1: GUI Temperature Calibration Sheet.
Typical set offset and span values are inserted as a reference.



Probe Name	Description	Raw Value	Offset	Span	Calculated
P 4-1	Top Product	670	2000	16000	20
P 4-2	Separator	1430	7100	32000	45.3
DP 3-1	Col C 3-2 DP	0	3200	16000	0

Figure C- 2: GUI Pressure Calibration Sheet.
Typical set offset and span values are inserted as a reference.

C.3 Pump calibrations

The pumps were calibrated using a measuring cylinder and a stopwatch. In order to determine the volumetric flow rate at a specific pump setting the pumps were turned on and set to a specific stroke length. The time it takes for the pump to fill a known volume was measured and the volumetric flow rate calculated. The raw data can be seen below in Table C- 2 with the fitted trend lines in Figure C- 3 for pump P 1-1 and Figure C- 4 for pump P 1-2.

The calibration curves were tested during experimentation by weighing the column overheads, bottoms and liquid hold-up over a run at a specific pump setting. The total mass is then calculated and divided by the runtime, after which the volumetric flow rate is calculated using the fluid density. The pump calibration curves were found to be accurate.

Table C- 2: Pump calibration data.

P 1–1 Small Capacity Diaphragm Pump				P 1–2 Large Capacity Piston Pump			
Pump stroke setting (mm)	Time measured (s)	Volume (ml)	Volumetric Rate (ml/s)	Pump stroke setting (mm)	Time measured (s)	Volume (ml)	Volumetric Rate (ml/s)
15	57.28	50	0.87	20	36.22	100	2.76
15	57.74	50	0.87	20	36	100	2.78
14	62.21	50	0.80	19	37.22	100	2.69
14	62.56	50	0.80	19	37.43	100	2.67
13	66.88	50	0.75	18	39.53	100	2.53
13	65.63	50	0.76	17	41.35	100	2.42
12	67.96	50	0.74	17	42.22	100	2.37
11	71.78	50	0.70	16	43.72	100	2.29
10	80.19	50	0.62	15	47	100	2.13
10	79.68	50	0.63	14	49.9	100	2.00
9	86.35	50	0.58	14	50.81	100	1.97
9	53.84	30	0.56	13	55.03	100	1.82
8	95.67	50	0.52	13	55.66	100	1.80
7	112.68	50	0.44	12	61.47	100	1.63
6	131.41	50	0.38	11	66.47	100	1.50
5	91.3	30	0.33	10	73.4	100	1.36
4	75.87	20	0.26	9	80.75	100	1.24
3	106.33	20	0.19	9	80.84	100	1.24
2	98.53	10	0.10	8	91	100	1.10
				7	102.87	100	0.97
				6	118.88	100	0.84
				5	141.79	100	0.71
				5	143.44	100	0.70
				4	178.53	100	0.56
				3	114.83	50	0.44
				2	169.24	50	0.30
				1	136.16	20	0.15

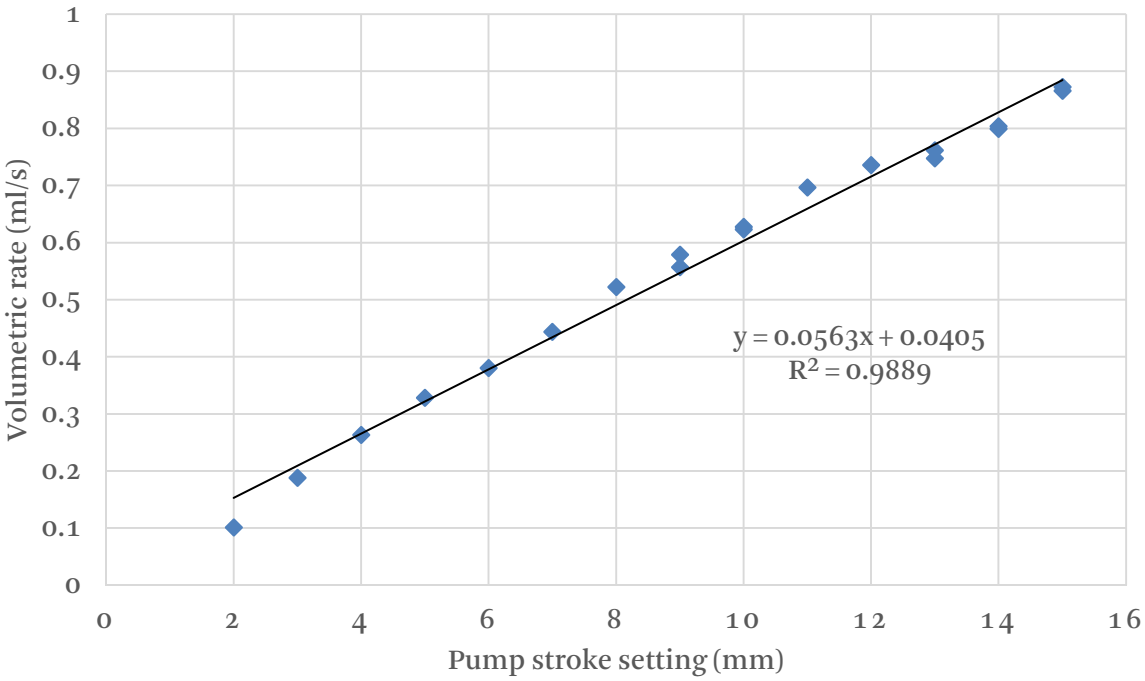


Figure C- 3: Calibration curve for volumetric flow from pump P 1-1.

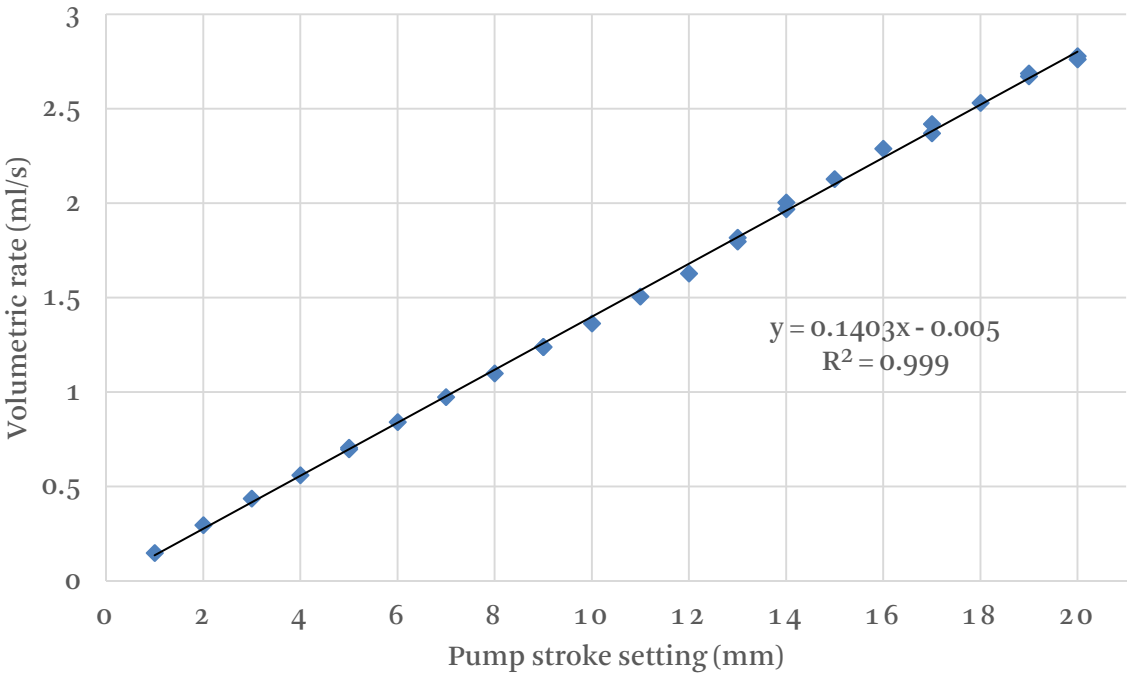


Figure C- 4: Calibration curve for volumetric flow from pump P 1-2.

C.4 Alarms and Safety Interlocks

All the alarms and safety interlocks, as discussed in the HAZOP in Appendix E, were tested individually. This was done by changing the alarm setpoint and cut-out values ambient conditions in order to trigger the relevant alarm. If this was not possible, as in the case of the level sensors and refrigeration system, the sensor was removed and manually triggered. All of the safety interlocks were tested successfully and returned to their set values. Typical set values can be seen in Appendix D, Figure D- 7 and Figure D- 8. The emergency stop button integrated into the plant HMI was also tested successfully.

C.5 Automation Sequences

The sequences, as described in Section 4.2.5, were all triggered individually and tested to see if they function correctly. No problems occurred.

C.6 Commissioning

C.6.1 Utility Commissioning

The heating and cooling utility systems function separately from the pilot plant, except for sharing an electrical supply, and could be commissioned separately and individually.

Each of the two heating systems were first commissioned individually. Each oil heater was flushed using excess Dowtherm heating oil to clean the heater tanks and pump. After this the heater tank was filled to maximum level. The pump was turned on, while leaving the heating elements off, with all the heating valves closed (See Section 4.2.1, Figure 4- 8, for the heating system PFD and valve specifications). Each of the heating sections were opened individually using the heating valves and inspected for any leaks. After any occurring leaks were seen to, all the valves were opened and the heating elements turned on at a low set point. The heating setpoint was then slowly increased to the maximum of 200°C while continually inspecting the system for leaks. After this the heating elements were turned off and the system allowed to return to room temperature overnight. After this the system was once again inspected for any leaks.

The refrigerator system was built into and connected to the new pilot plant with the help of Azure Refrigeration. After the installation of the required piping by Azure the system was pressurised with nitrogen and tested for leaks. Any occurring leaks were fixed and the system was repressurised and left overnight to test for any pressure drop. The system showed no signs of pressure drop the system was drained and a vacuum pump applied overnight to draw a

vacuum. After a vacuum was drawn the system was again closed and left overnight to test if any leaks cause loss of vacuum. No vacuum loss occurred and Azure Refrigeration returned to perform the loading of the refrigerant gas. The gas was loaded and the system was turned on and allowed to run for several hours. The system showed rapid cooling and operated without any problems.

C.6.2 Cleaning and Flushing

The process side of the pilot plant was fully cleaned and flushed before commissioning. Although care was taken during construction to keep components clean, this is not sufficient to guarantee a clean process environment. To remedy this the system was first rinsed, using the process pumps, with warm soapy water followed by several clean water cycles. After this the system was dried overnight using compressed air. After loading the packing the system was then rinsed using methanol to remove any remaining residues. Process valves were cycled and strategic couplings opened to ensure the methanol reached the whole of the system. The system was then drained and once again flushed and dried using compressed air.

C.6.3 Pilot Plant Pressure Testing

Apart from the vessels that were pressure tested by RITC the system as a whole was also tested using clean water and a dead weight tester. After fixing a leak in the system the pressure was left on overnight. No pressure loss was observed and the system was deemed ready for experimentation.

C.6.4 Pilot Plant Commissioning

For initial commissioning the system was prepared according to the start-up procedure discussed in Appendix F, F.2, using only CO_2 with no liquid feed. The column temperature was kept at approximately 40°C with the separator at 50°C. The column operating pressure was increased stepwise from gas bottle pressure up to 280 bar, monitoring the system for any irregularities before moving from one step to the next. During this process the system was continually tested for leaks.

After fixing a small leak found, the system was returned to gas bottle pressure. Each of the sections were isolated at pressure using process valves and left overnight. The next day each section was inspected for pressure loss. Noting no significant pressure loss, the system was deemed ready for experimentation.

Appendix D: Main GUI Screens

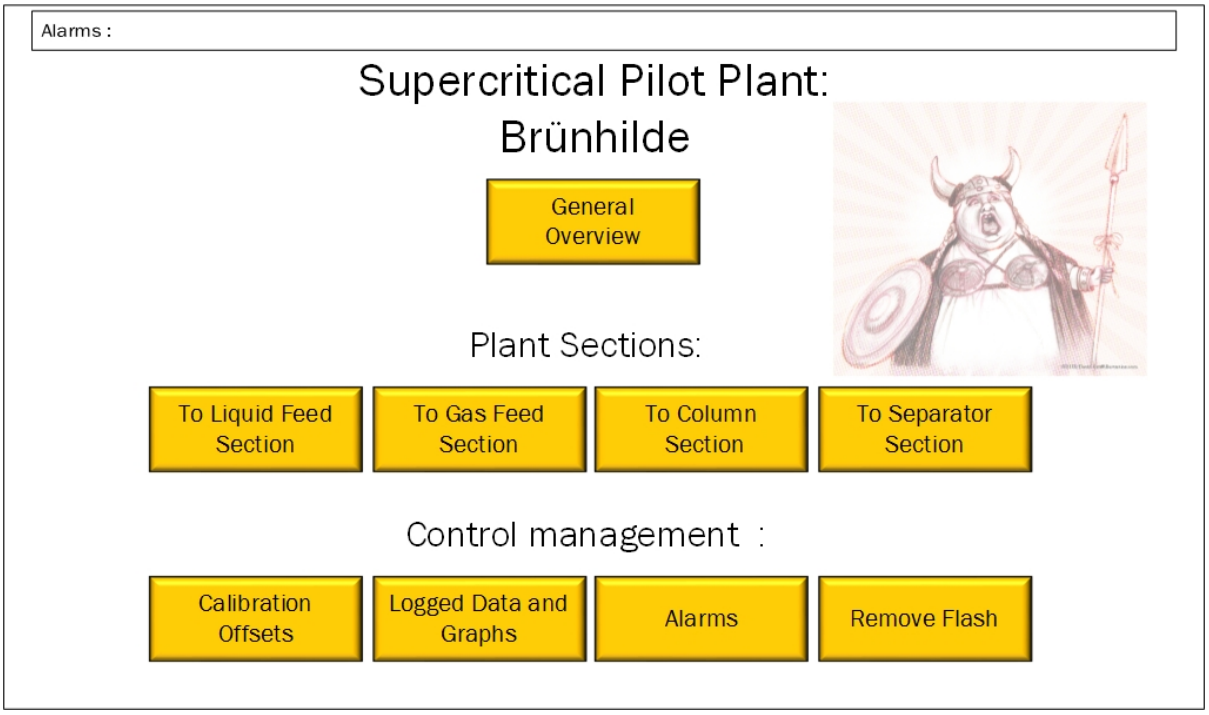


Figure D- 1: GUI Main or 'Home' screen.
Provides links to the main sections.

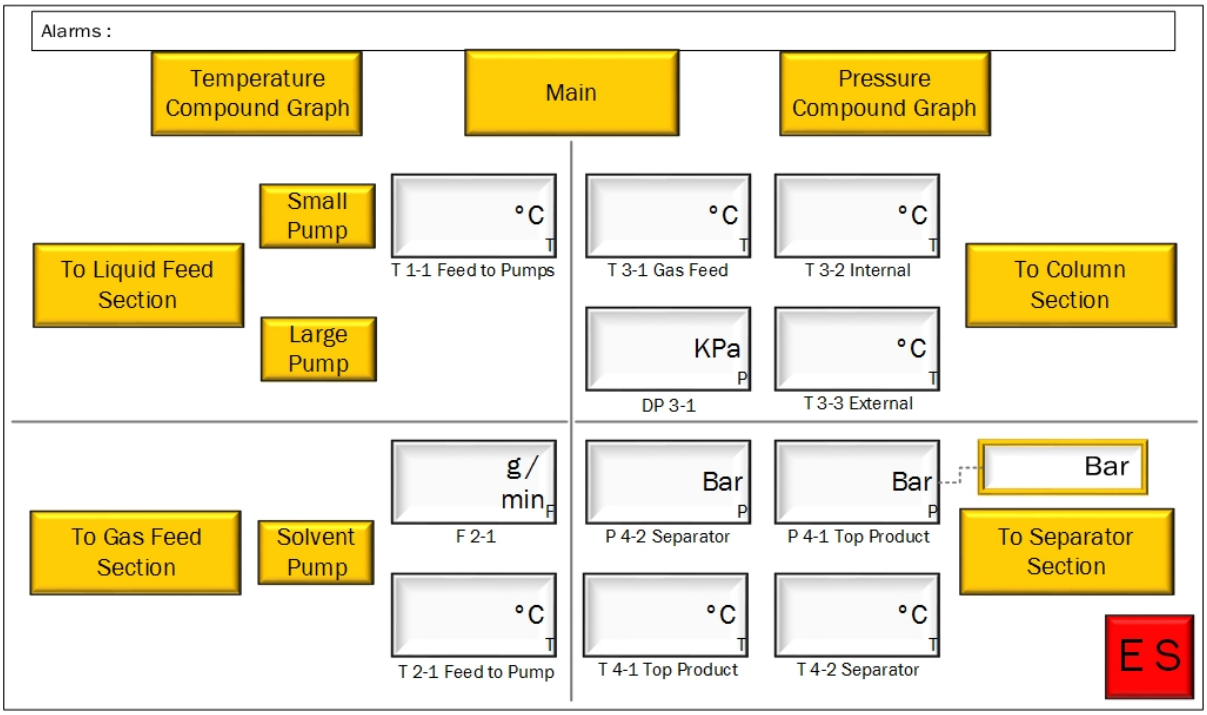


Figure D- 2: GUI General Overview screen.
Provides an overview of all the electronic measurements and control of the pumps and column setpoint.

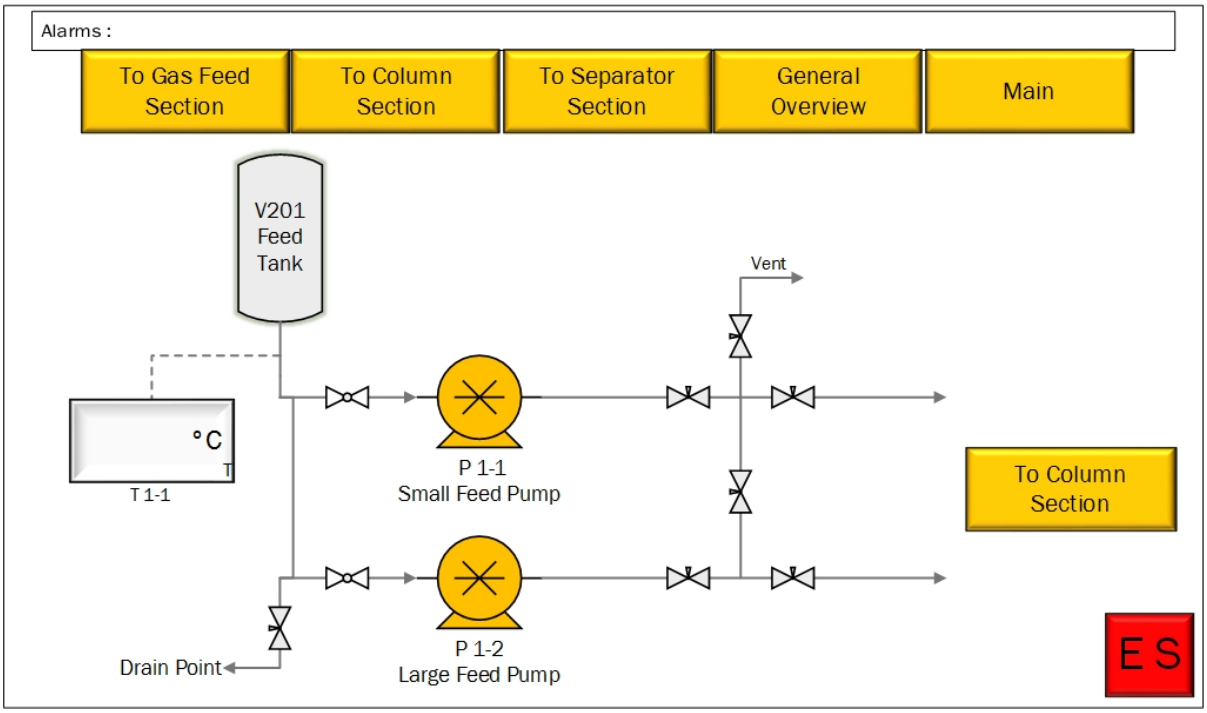


Figure D- 3: GUI Liquid Feed Section.
Shows the liquid feed section and allows the user to control the two liquid feed pumps.

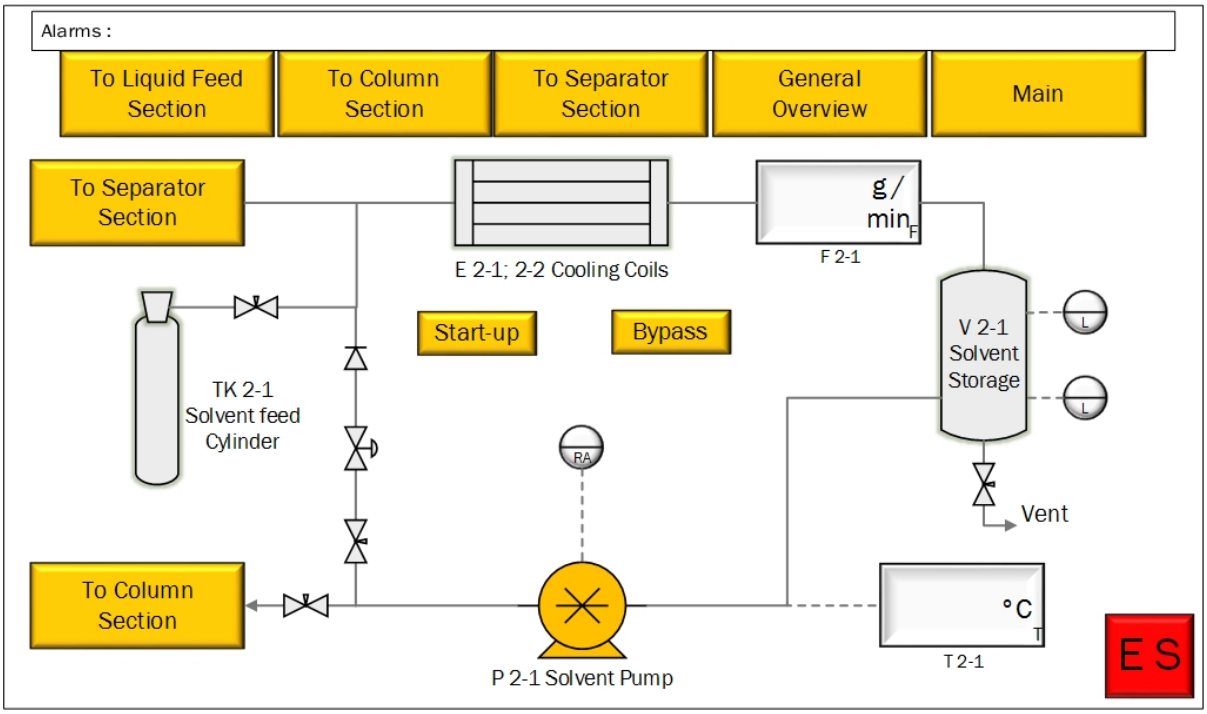


Figure D- 4: GUI Gas Feed Section.
Shows the liquid feed section and allows the user to control the solvent pump. The start- up and bypass sequences is accessed from this screen.

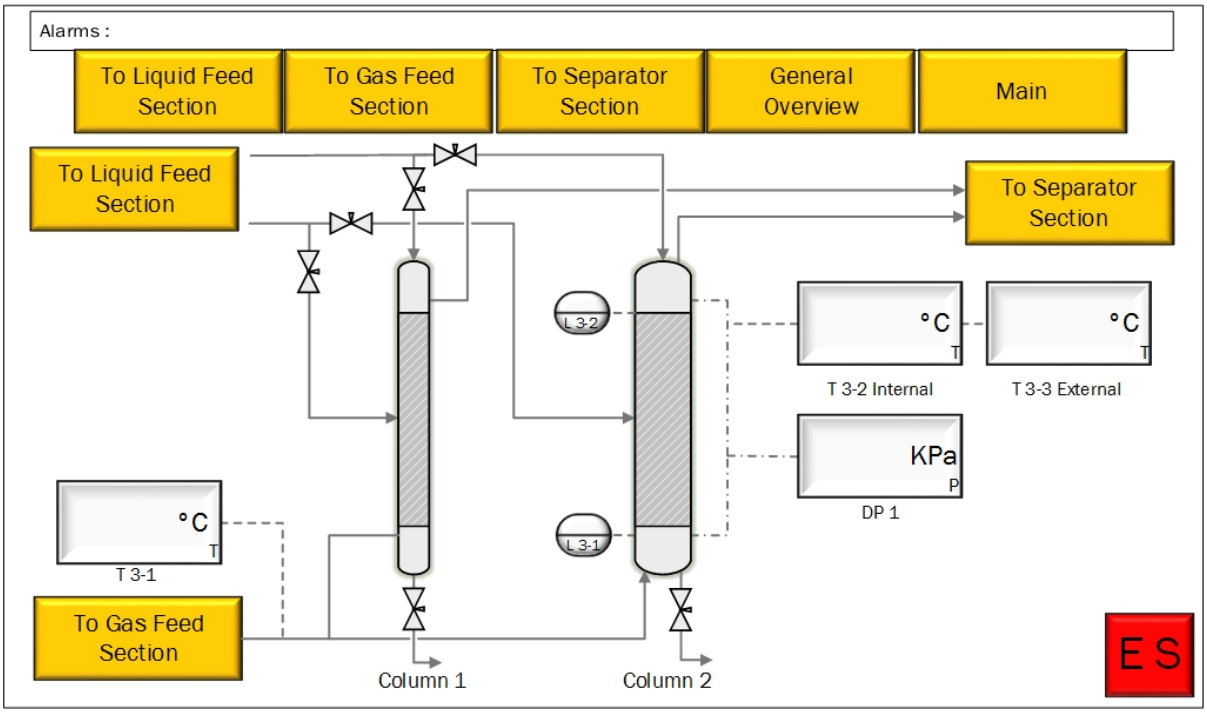


Figure D- 5: GUI Column Section.
Shows the column section.

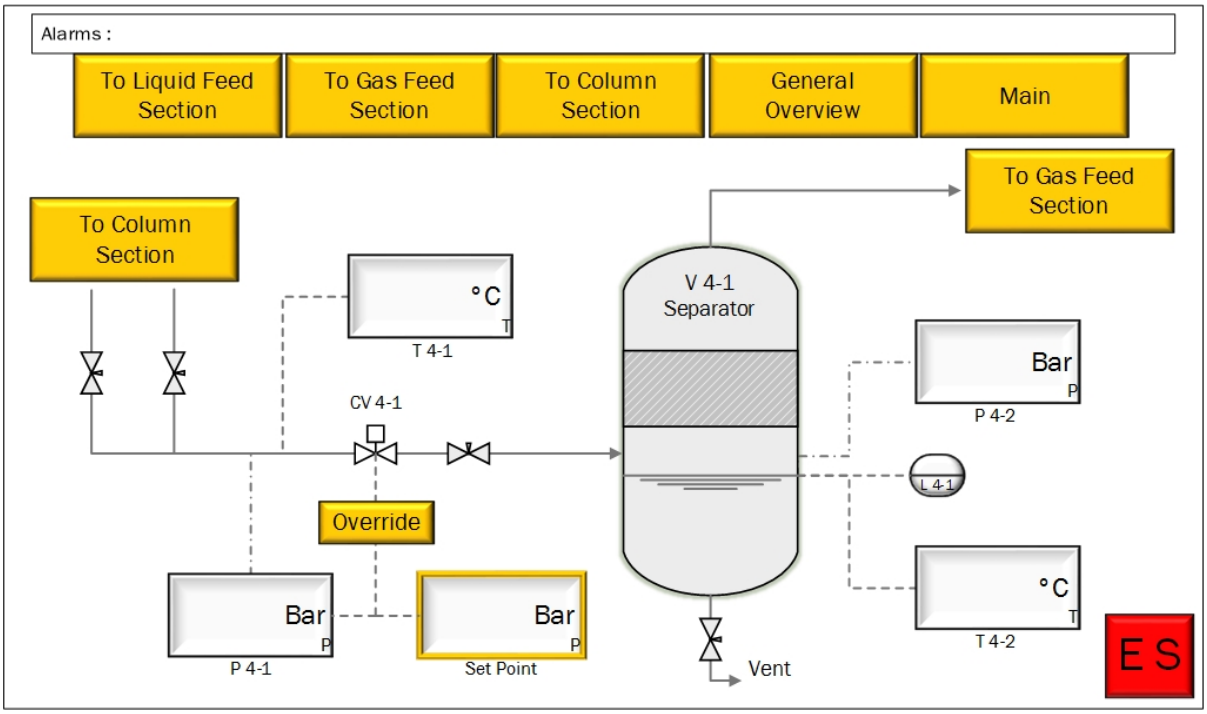
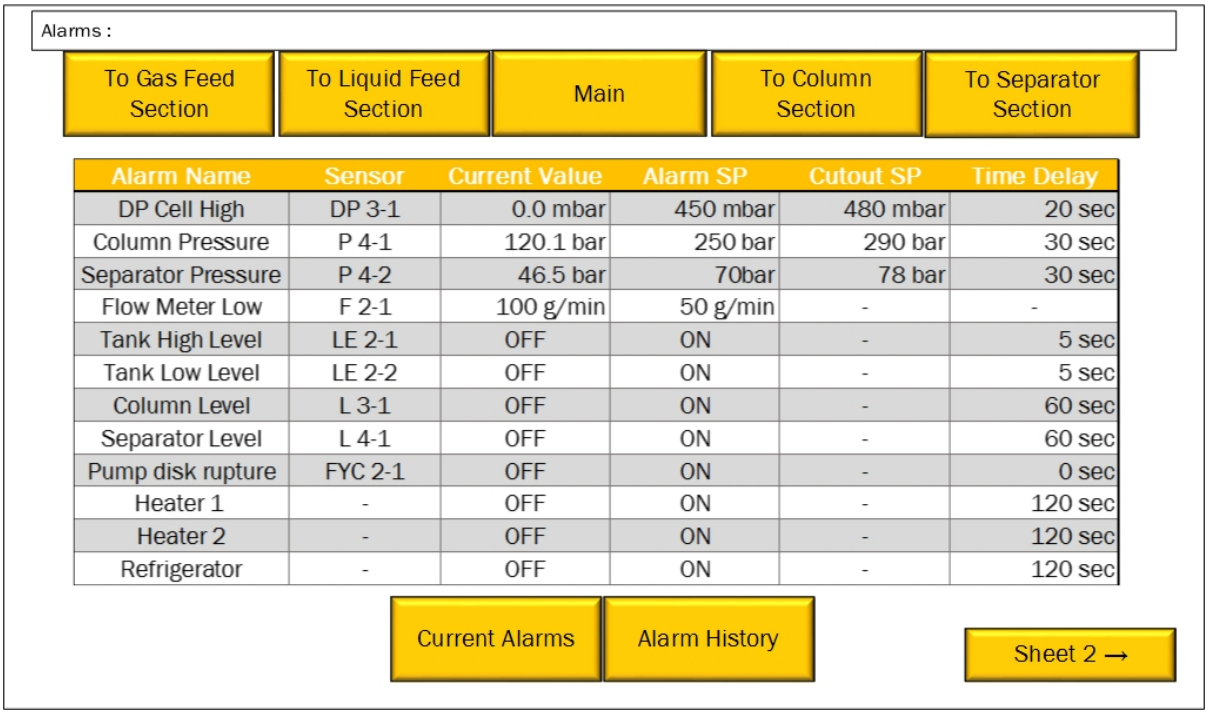
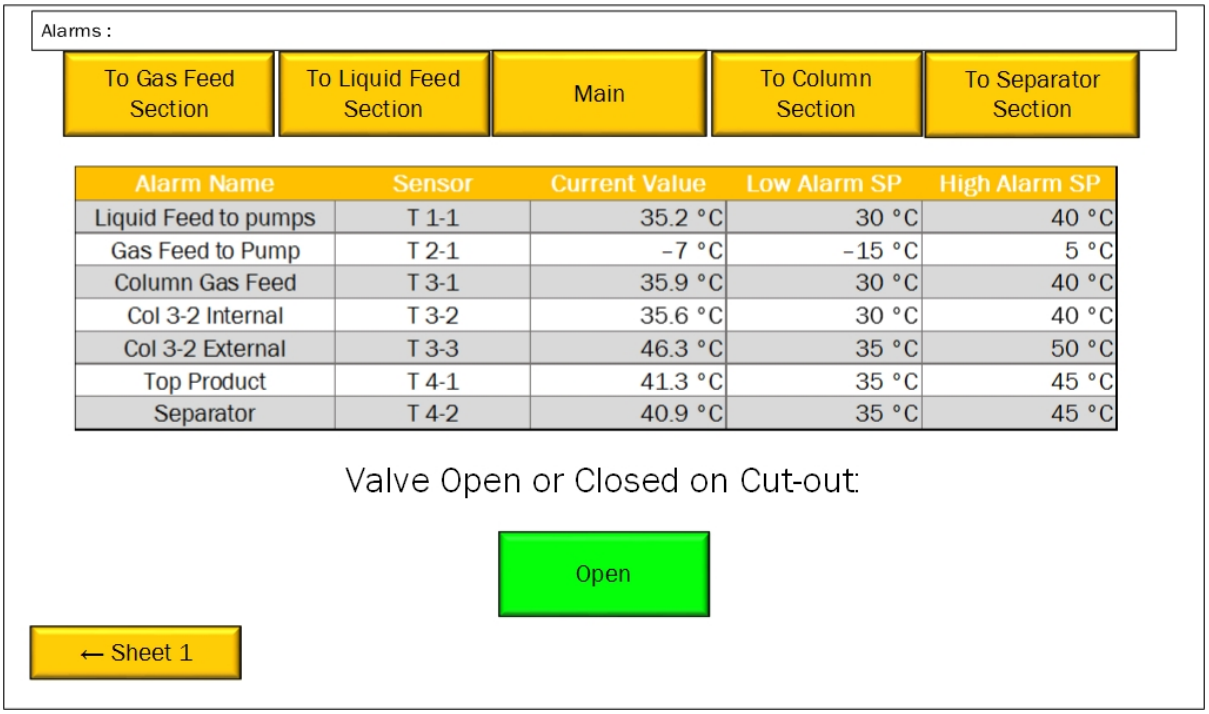


Figure D- 6: GUI Separator Section.
Shows the separator section and allows the user to control the control valve set point. The control valve override is accessed from this screen.



Alarm Name	Sensor	Current Value	Alarm SP	Cutout SP	Time Delay
DP Cell High	DP 3-1	0.0 mbar	450 mbar	480 mbar	20 sec
Column Pressure	P 4-1	120.1 bar	250 bar	290 bar	30 sec
Separator Pressure	P 4-2	46.5 bar	70bar	78 bar	30 sec
Flow Meter Low	F 2-1	100 g/min	50 g/min	-	-
Tank High Level	LE 2-1	OFF	ON	-	5 sec
Tank Low Level	LE 2-2	OFF	ON	-	5 sec
Column Level	L 3-1	OFF	ON	-	60 sec
Separator Level	L 4-1	OFF	ON	-	60 sec
Pump disk rupture	FYC 2-1	OFF	ON	-	0 sec
Heater 1	-	OFF	ON	-	120 sec
Heater 2	-	OFF	ON	-	120 sec
Refrigerator	-	OFF	ON	-	120 sec

Figure D- 7: GUI Alarm Sheet 1.
Shows the first alarm configuration sheet with the pressure, flow, level and utility alarms. Typical set point values are inserted as a reference.



Alarm Name	Sensor	Current Value	Low Alarm SP	High Alarm SP
Liquid Feed to pumps	T 1-1	35.2 °C	30 °C	40 °C
Gas Feed to Pump	T 2-1	-7 °C	-15 °C	5 °C
Column Gas Feed	T 3-1	35.9 °C	30 °C	40 °C
Col 3-2 Internal	T 3-2	35.6 °C	30 °C	40 °C
Col 3-2 External	T 3-3	46.3 °C	35 °C	50 °C
Top Product	T 4-1	41.3 °C	35 °C	45 °C
Separator	T 4-2	40.9 °C	35 °C	45 °C

Figure D- 8: GUI Alarm Sheet 2.
Shows the second alarm configuration sheet with the temperature alarms. The control valve position state during a cut-out can also be selected. Typical set point values are inserted as a reference.

Appendix E: HAZOP

The HAZOP study was performed using the guidelines and principles provided by Turton, et al. (55). Deviations in pressure, temperature, and flow were considered using the keywords, NO, LOW and HIGH. Below, each of the major elements of the pilot plant are considered individually according to specified procedures.

Table E- 1: HAZOP table for Liquid Feed Tank V 1-1.

Process unit:		V 1–1 [Feed Tank]		
Intention:		To store and provide liquid feed to the liquid feed pumps		
Standard operation:		Atmospheric with batch wise loading. Max temp 200 °C		
Guide Word	**Deviation**	**Cause**	**Consequences**	**Action**
No	Flow	Blockage in effluent line	No liquid flow to pumps or column	Inspect and unblock effluent line
Low	Temperature	Temperature valves TV 1, 2, 3 and/or 4 closed or partially closed	Incorrect liquid feed temperature	Alarm on T 1–1 will indicate a temperature outside range. Check temperature valves TV 1, 2, 3 and/or 4
↑	↑	Three–way temperature valves TTV 1, 2 closed or incorrect	↑	Alarm on T 1–1 will indicate a temperature outside range. Check three way temperature valves TTV 1, 2
↑	↑	Wrong setting or faulty heater H1/H2	↑	Alarm on T 1–1 will indicate a temperature outside range. Check heater H1/H2. Alarm on heater will indicate a faulty heater
High	Temperature	Wrong setting on heater H1/H2	Incorrect liquid feed temperature	Alarm on T 1–1 will indicate a temperature outside range. Check heater H1/H2

Table E- 2: HAZOP table for Small Capacity Feed Pump P 1-1.

Process unit:	P 1–1 [Small Capacity Feed Pump]			
Intention:	Pumping liquid feed to column at high operating pressure			
Standard operation:	Up to 2ℓ/h rate, 200 °C and 300 bar			
Guide Word	**Deviation**	**Cause**	**Consequences**	**Action**
No	Flow	Pump P 1–1 Faulty	No liquid flow in column	Stop process and inspect pump P 1–1
↑	↑	No liquid in V 1–1	↑	Check and refill feed vessel V 1–1
↑	↑	Valve BV 1–1 closed	↑	Check valve BV 1–1
↑	↑	Blockage in upstream line	↑	Inspect and unblock feed line
Low	Flow	Pump P 1–1 on wrong setting	Incorrect liquid feed rate to column	Check the manual flow setting on pump P 1–1
↑	↑	Valve BV 1–1 not fully open	↑	Check valve BV 1–1
↑	↑	Low pressure head due to viscous liquid	↑	Apply back pressure to feed vessel V 1–1
↑	Temperature	Temperature valve TV 1, 3 and/or 4 closed or partially closed	Incorrect liquid feed temperature	Alarm on T 1–1 will indicate a temperature outside range. Check temperature valve TV 1, 3 and/or 4
↑	↑	Three–way temperature valves TTV 1, 2 closed or incorrect	↑	Alarm on T 1–1 will indicate a temperature outside range. Check three way temperature valves TTV 1, 2
↑	↑	Wrong setting or faulty heater H1/H2	↑	Alarm on T 1–1 will indicate a temperature outside range. Check heater H1/H2. Alarm on heater will indicate a faulty heater

(Table E- 2 continues)

Guide Word	Deviation	Cause	Consequences	Action
High	Flow	Pump P 1–1 on wrong setting	Incorrect liquid feed rate to column	Check the manual flow setting on pump P 1–1
↑	Temperature	Wrong setting on heater H1/H2	Incorrect liquid feed temperature	Alarm on T 1–1 will indicate a temperature outside range. Check heater H1/H2
↑	Pressure	Blockage in downstream line	Pressure build–up	Shut down pump P 1–1. Vent the excess pressure. Inspect and unblock downstream line. In extreme cases burst disk BD 1–1 will burst.
↑	↑	Closed valve to column feed	Incorrect liquid feed temperature	Shut off pump P 1–1. Open the relevant valves for top or middle column feed. If this does not immediately remedy the situation vent excess pressure. In extreme cases burst disk BD 1–1 will burst.

Table E- 3: HAZOP table for Large Capacity Feed Pump P 1-2.

Process unit:		P 1–2 [Large Capacity Feed Pump]		
Intention:		Pumping liquid feed to column at high operating pressure		
Standard operation:		Up to 8ℓ/h rate, 200 °C and 300 bar		
Guide Word	**Deviation**	**Cause**	**Consequences**	**Action**
No	Flow	Pump P 1–2 Faulty	No liquid flow in column	Stop process and inspect the pump P 1–2. In case of diaphragm rupture alarm on FYC 2–1 will immediately shut off system
↑	↑	No liquid in V 1–1	↑	Check and refill feed vessel V 1–1
↑	↑	Valve BV 1–2 closed	↑	Check valve BV 1–2
↑	↑	Blockage in upstream line	↑	Inspect and unblock feed line
Low	Flow	Pump P 1–2 on wrong setting	Incorrect liquid feed rate to column	Check the manual flow setting on pump P 1–2
↑	↑	Valve BV 1–2 not fully open	↑	Check valve BV 1–2
↑	↑	Low pressure head due to viscous liquid	↑	Apply pressure to feed vessel V 1–1
↑	Temperature	Temperature valves TV 2, 3 and/or 4 closed or partially closed	Incorrect liquid feed temperature	Alarm on T 1–1 will indicate a temperature outside range. Check temperature valves TV 2, 3 and/or 4
↑	↑	Three–way temperature valves TTV 1, 2 closed or incorrect	↑	Alarm on T 1–1 will indicate a temperature outside range. Check three way temperature valves TTV 1, 2
↑	↑	Wrong setting or faulty heater H1/H2	↑	Alarm on T 1–1 will indicate a temperature outside range. Check heater H1/H2. Alarm on heater will indicate a faulty heater.

(Table E- 3 continues)

Guide Word	Deviation	Cause	Consequences	Action
High	Flow	Pump P 1–2 on wrong setting	Incorrect liquid feed rate to column	Check the manual flow setting on pump P 1–2
↑	Temperature	Wrong setting on heater H1/H2	Incorrect liquid feed temperature	Alarm on T 1–1 will indicate a temperature outside range. Check heater H1/H2
↑	Pressure	Blockage in downstream line	Pressure build–up	Shut down pump P 1–2. Vent the excess pressure. Inspect and unblock downstream line. In extreme cases burst disk BD 1–1 will burst.
↑	↑	Closed valve to column feed	Incorrect liquid feed temperature	Shut off pump P 1–2. Open the relevant valves for top or middle column feed. If this does not immediately remedy the situation vent excess pressure. In extreme cases burst disk BD 1–1 will burst.

Table E- 4: HAZOP table for Water Pre-cooler E 2-1, Chilled Condensor E 2- 2 and Mass Flow Meter M 2-1.

Process unit:	E 2–1 [Water Pre–cooler], E 2–2 [Chilled Condenser] and M 2–1 [Mass Flow Meter]			
Intention:	Cooling and condensing the fresh / recycled solvent before pumping. Measuring the mass flow rate of solvent			
Standard operation:	Up to 80 bar and between 200 and –10 °C			
Guide Word	**Deviation**	**Cause**	**Consequences**	**Action**
No	Flow	Valve NV 2–1 closed	No fresh solvent flow	Alarm on F 2–1 will go off. Check valve NV 2–1
↑	↑	Valve NV 4–4 closed	No solvent flow to buffer tank V 2–1	Alarm on F 2–1 will go off. Check valve NV 4–4
↑	↑	Valves SV 2–1 and/or NV 2–3 closed	↑	Alarm on F 2–1 will go off. Check valves SV 2–1 and NV 2–3
↑	↑	Blockage in upstream line	↑	Alarm on F 2–1 will go off. Inspect and unblock upstream line
↑	↑	Blockage in exchanger	↑	Alarm on F 2–1 will go off. Inspect and unblock exchanger
Low	Flow	Valve NV 2–1 not fully open	Incorrect solvent feed rate to buffer tank V 2–1	Check valve NV 2–1
↑	↑	Valve NV 4–4 closed	↑	Check valve NV 4–4
↑	↑	Valves SV 2–1 and/or NV 2–3 closed	↑	Check valves SV 2–1 and NV 2–3
↑	↑	Insufficient amount of solvent in the system	↑	Check solvent level in solvent buffer tank V 2–1. Change solvent feed cylinder TK 2–1
↑	↑	Insufficient condensation of solvent	↑	See low pressure

(Table E- 4 continues)

Guide Word	Deviation	Cause	Consequences	Action
Low	Temperature	Refrigerator R1 set too low	Incorrect liquid feed temperature. Icing of liquid	Picked up by alarm on T 2–1. Check refrigerator R1
↑	Pressure	Insufficient amount of solvent in the system	Insufficient condensation of solvent	Check solvent level in solvent buffer tank V 2–1. Check / change solvent feed cylinder TK 2–1
↑	↑	Valve RV 2–2 and/or NV 2–4 open	Lack op pressure build–up	Check valves RV 2–2 and NV 2–4
High	Temperature	Refrigerator R1 set too high or faulty	Incorrect liquid feed temperature. Insufficient condensation of solvent	Picked up by alarm on T 2–1. Check refrigerator R1. Alarm on refrigerator may also indicate a fault
↑	↑	Cooling water valves UV 1 and/or UV 2 closed or partially closed	↑	Check valves UV 1 and UV 2
↑	Pressure	Excessive solvent in system	Pressure build–up	Pressure relief valve RV 2–2 will open. Check solvent level in solvent buffer tank V 2–1
↑	↑	Pump P 2–1 faulty or off	↑	Check pump P2–1
↑	↑	Blockage in downstream line	↑	Pressure relief valve RV 2–2 will open. Inspect and unblock downstream line

Table E- 5: HAZOP table for Solvent Buffer Tank V 2-1.

Process unit:	V 2–1 [Solvent Buffer Tank]			
Intention:	Provides a liquid solvent buffer to pump P 2–1 and used to store solvent.			
Standard operation:	Up to 80 bar and –10 °C			
Guide Word	**Deviation**	**Cause**	**Consequences**	**Action**
No	Flow	Blockage in upstream line	No flow to pump P 2–1	Inspect and unblock feed line
↑	↑	Valve NV 2–5 closed	↑	Check valve NV 2–5
Low	Temperature	Excessive cooling in E 2–2	Incorrect liquid feed temperature	Picked up by alarm on T 2–1. Check chilled condenser E 2–2
↑	Level	Insufficient amount of solvent in the system	Interruption of experiment due to low level. Possible pump P2–1 malfunction	Low level alarm LE 2–2 will shut off system after a set time. Check valve NV 2–1. Check / change solvent feed cylinder TK 2–1
↑	↑	Insufficient condensation of solvent	↑	Low level alarm LE 2–2 will shut off system after a set time. Check E 2–1 and E 2–2
↑	↑	Valve NV 2–4 open	Loss of solvent to atmosphere	Low level alarm LE 2–2 will shut off system after a set time. Check valve NV 2–4

(Table E- 5 continues).

Guide Word	Deviation	Cause	Consequences	Action
High	Temperature	Insufficient cooling in E 2–1 and E 2–2	Incorrect liquid feed temperature. Insufficient condensation of solvent.	Picked up by alarm on T 2–1. Check coolers E 2–1 and condenser E 2–2
↑	Level	Excessive solvent in system	Pressure build–up in system	High level alarm LE 2–1 will shut off system after a set time. Vent excess solvent by opening NV 2–4
↑	↑	Valve NV 2–5 closed	Solvent flooding	High level alarm LE 2–1 will shut off system after a set time. Check and open valve NV 2–5
↑	↑	Blockage in downstream line	↑	High level alarm LE 2–1 will shut off system after a set time. Check and unblock downstream line
↑	↑	Pump P 2–1 faulty or off	↑	High level alarm LE 2–1 will shut off system after a set time. Check pump P2–1

Table E- 6: HAZOP table for Regulator Valve SV 2-1, Recycle Cut-off Valve NV 2-3 and Recycle Loop.

Process unit:	SV 2–1 [Regulator Valve], NV 2–3 [Recycle Cut–off Valve] and Recycle Loop			
Intention:	Recycle the high pressure liquid solvent back for start–up or low flow conditions			
Standard operation:	Up to 100 bar, –10 °C			
Guide Word	**Deviation**	**Cause**	**Consequences**	**Action**
No	Flow	Blockage downstream	No solvent recycle	Check and unblock downstream line
↑	↑	Pump P 2–1 faulty or off	↑	Check pump P2–1
High	Pressure	SV 2–1 opened too much	High pressure enters low pressure section	Pressure relief valve RV 2–1 will open. Tune SV 2–1 to appropriate setting

Table E- 7: HAZOP table for Pump feed Chilled Pre-cooler E 2-3.

Process unit:	E 2–3 [Pump Feed Chilled Pre–cooler]			
Intention:	Precooling the liquid solvent before being pumped			
Standard operation:	Up to 100 bar, –10 °C			
Guide Word	**Deviation**	**Cause**	**Consequences**	**Action**
No	Flow	Valve NV 2–5 closed	No solvent flow to pump P 2–1 and column section	Check valve NV 2–5
↑	↑	Pump P 2–1 faulty or off	↑	Check pump P2–1
↑	↑	No liquid in solvent buffer tank V 2–1	↑	Check solvent buffer tank V 2–1
↑	↑	Blockage in upstream line	↑	Inspect and unblock upstream line
Low	Flow	Valve NV 2–5 not fully open.	Throttling of solvent feed to pump P 2–1	Check valve NV 2–5
↑	Temperature	Refrigerator R1 set too low	Incorrect liquid feed temperature. Icing of liquid feed	Alarm on T 2–1 will indicate a temperature outside range. Check refrigerator R1
High	Temperature	Refrigerator R1 set too high or faulty	Incorrect liquid feed temperature. Pump cavitation.	Alarm on T 2–1 will indicate a temperature outside range. Check refrigerator R1. Alarm on refrigerator will indicate a fault

Table E- 8: HAZOP table for Solvent Feed Pump P 2-1.

Process unit:	P 2–1 [Solvent Feed Pump]			
Intention:	Pumps the liquid solvent to the column at high pressure			
Standard operation:	Up to 55 ℓ/h rate, –10 °C and 300 bar			
Guide Word	**Deviation**	**Cause**	**Consequences**	**Action**
No	Flow	Pump P 2–1 Faulty	No solvent flow to column	Stop process and inspect the pump P 2–1. Rupture alarm installed to stop the plant in case of pump diaphragm failure
↑	↑	No liquid in solvent buffer tank V 2–1	↑	Check solvent buffer tank V 2–1
↑	↑	Valve NV 2–5 closed	↑	Check valve NV 2–5
↑	↑	Blockage in upstream line	↑	Inspect and unblock feed line
Low	Flow	Pump P 2–1 on wrong setting	Incorrect solvent feed rate to column	Check the manual flow setting on pump P 2–1
↑	↑	Valve NV 2–5 not fully open	↑	Check valve NV 2–5
↑	Temperature	Refrigerator R1 set too low	Incorrect liquid feed temperature. Icing of liquid	Alarm on T 2–1 will indicate a temperature outside range. Check refrigerator R1
High	Flow	Pump P 2–1 on wrong setting	Incorrect liquid feed rate to column	Check the manual flow setting on pump P 2–1
↑	Temperature	Refrigerator R1 set too high or faulty	Incorrect liquid feed temperature	Alarm on T 2–1 will indicate a temperature outside range. Check refrigerator R1. Alarm on refrigerator will indicate a fault

Table E- 9: HAZOP table for Solvent Heater E 3-1.

Process unit:	E 3–1 [Solvent Heater (Tracing)]			
Intention:	Heats the solvent to operating temperatures			
Standard operation:	Up to 200 °C and 300 bar			
Guide Word	**Deviation**	**Cause**	**Consequences**	**Action**
No	Flow	Blockage in upstream line	No Solvent flow to columns	Inspect and unblock upstream line
↑	↑	Pump P 2–1 faulty or off	↑	Check pump P2–1
↑	↑	Valve NV 3–1 or N3–2 closed	↑	Check valves NV 3–1 and NV 3–2
↑	↑	Valve NV 2–2 closed	↑	Check valve NV 2–2
Low	Flow	Valve NV 3–1 or N3–2 not fully open	Incorrect solvent feed rate to column	Check valves NV 3–1 and NV 3–2
↑	↑	Valve NV 2–2 not fully open	↑	Check valve NV 2–2
↑	↑	Pump P 2–1 on wrong setting	↑	Check the manual flow setting on pump P 2–1
↑	Temperature	Wrong setting or faulty heater H1	Incorrect solvent temperature to column.	Alarm on T 3–1 will indicate a temperature outside range. Check heater H1. Alarm on heater will indicate a faulty heater
High	Temperature	Wrong setting on heater H1	Incorrect solvent temperature to column.	Alarm on T 3–1 will indicate a temperature outside range. Check heater H1
↑	Pressure	Blockage in downstream line or column	Pressure build–up	Shut off pump P 2–1. Vent excess pressure. Inspect and unblock downstream line. In extreme cases burst disk BD 3–1 will burst.
↑	↑	Valve NV 3–1 or N 3–2 closed	↑	Shut off pump P 2–1. Open valve NV 3–1 or N 3–2. If this does not immediately remedy the situation vent excess pressure. In extreme cases burst disk BD 3–1 will burst.

Table E- 10: HAZOP table for Small Diameter Column C 3-1 and column feed lines.

Process unit:	C 3–1 [Small Diameter Column] – Includes column feed lines			
Intention:	Column to effect mass transfer or phase interaction			
Standard operation:	Up to 200 °C and 300 bar			
Guide Word	**Deviation**	**Cause**	**Consequences**	**Action**
No	Flow (Liquid)	Liquid feed pump P 1–1 or P 1–2 off or faulty	No liquid flow in column	Check pump P 1–1 or P 1–2
↑	↑	Incorrect feed valve selection setup.	↑	Check liquid feed valve assembly
↑	↑	Valve NV 3–6 or 3–8 closed	↑	Check valve NV 3–6 or NV 3–8
↑	↑	Blockage in upstream line	↑	Inspect and unblock upstream line
↑	↑	Blockage in column packing	↑	Inspect and unblock column
↑	Flow (Solvent)	Solvent feed pump P 2–1 off or faulty	No solvent flow in column	Check pump P 2–1
↑	↑	Valve NV 3–1 or NV 3–9 closed	↑	Check valves NV 3–1 and NV 3–9
Low	Flow (Liquid)	Pump P 1–1 or P 1–2 on wrong setting	Incorrect liquid flow in the column	Check the manual flow setting on pump P 1–1 or P 1–2
↑	↑	Upstream valves not fully open	↑	Check upstream valves
↑	Temperature	Wrong setting or faulty heater H1	Incorrect column temperature	Check heater H1. Alarm on heater will indicate a faulty heater
↑	↑	Temperature valves TV 5, 7 and/or 9 closed or partially closed	↑	Check temperature valves TV 5, 7 and/or 9
↑	Pressure	Control valve CV 4–1 faulty or at too low setpoint	Incorrect column pressure	Check control valve CV 4–1 and control panel setpoint

(Table E- 10 Continues)

Guide Word	Deviation	Cause	Consequences	Action
High	Temperature	Wrong setting on heater H1	Incorrect column temperature	Check heater H1
↑	Pressure	Valve NV 3–9 or NV 4–1 not fully open or closed	Pressure build–up	Alarm on P 4–1 will shut off system. Otherwise immediately shut off pumps. Open valve NV 3–9 or N 4–1. If this does not immediately remedy the situation vent excess pressure. Pressure relief valve RV 3–1 will open for pressures exceeding 300 bar.
↑	↑	Control valve CV 4–1 faulty or at too high setpoint	↑	Check control valve CV 4–1 and control panel setpoint
↑	↑	Blockage in downstream line	↑	Alarm on P 4–1 may shut off system. Otherwise immediately shut off pumps. Vent excess pressure. Inspect and unblock downstream line. Pressure relief valve RV 3–1 will open for pressures exceeding 300 bar.
↑	↑	Blockage in column packing	↑	Alarm on P 4–1 may shut off system. Otherwise immediately shut off pumps. Vent excess pressure. Inspect and unblock downstream line. Pressure relief valve RV 3–1 will open for pressures exceeding 300 bar.
↑	Liquid level	Infrequent draining	Liquid build–up in column	Periodically drain liquid holdup from the column

Table E- 11: HAZOP table for Large Diameter Column C 3-1 and column feed lines.

Process unit:		C 3–2 [Large Diameter Column] – Includes column feed lines		
Intention:		Column to effect mass transfer or phase interaction		
Standard operation:		Up to 200 °C and 300 bar		
Guide Word	**Deviation**	**Cause**	**Consequences**	**Action**
No	Flow (Liquid)	Liquid feed pump P 1–1 or P 1–2 off or faulty	No liquid flow in column	Check pump P 1–1 or P 1–2
↑	↑	Incorrect feed valve selection setup.	↑	Check liquid feed valve assembly
↑	↑	Valve NV 3–5 or 3–7 closed	↑	Check valve NV 3–5 or NV 3–7
↑	↑	Blockage in upstream line	↑	Inspect and unblock upstream line
↑	↑	Blockage in column packing	↑	Inspect and unblock column
↑	Flow (Solvent)	Solvent feed pump P 2–1 off or faulty	No solvent flow in column	Check pump P 2–1
↑	↑	Valve NV 3–2 or NV 3–9 closed	↑	Check valves NV 3–2 and NV 3–9
Low	Flow (Liquid)	Pump P 1–1 or P 1–2 on wrong setting	Incorrect liquid flow in the column	Check the manual flow setting on pump P 1–1 or P 1–2
↑	↑	Upstream valves not fully open	↑	Check upstream valves
↑	Temperature	Wrong setting or faulty heater H1	Incorrect column temperature	Alarm on T 3–2 will indicate a temperature outside range. Check heater H1. Alarm on heater will indicate a faulty heater
↑	↑	Temperature valve TV10 closed or partially closed	↑	Alarm on T 3–2 will indicate a temperature outside range. Check temperature valve TV
↑	Pressure	Control valve CV 4–1 faulty or at too low setpoint	Incorrect column pressure	Check control valve CV 4–1 and control panel setpoint

(Table E- 11 continues)

Guide Word	Deviation	Cause	Consequences	Action
High	Temperature	Wrong setting on heater H1	Incorrect column temperature	Alarm on T 3–2 will indicate a temperature outside range. Check heater H1
↑	Pressure	Valve NV 3–10 or NV 4–1 not fully open or closed	Pressure build–up	Alarm on P 4–1 will shut off system. Otherwise immediately shut off pumps. Open valve NV 3–10 or N 4–1. If this does not immediately remedy the situation vent excess pressure. Pressure relief valve RV 3–1 will open for pressures exceeding 300 bar.
↑	↑	Control valve CV 4–1 faulty or at too high setpoint	↑	Alarm on P 4–1 may shut off system. Check control valve CV 4–1 and control panel setpoint
↑	↑	Blockage in downstream line	↑	Alarm on P 4–1 may shut off system. Otherwise immediately shut off pumps. Vent excess pressure. Inspect and unblock downstream line. Pressure relief valve RV 3–1 will open for pressures exceeding 300 bar.
↑	↑	Blockage in column packing	↑	Alarm on P 4–1 may shut off system. Otherwise immediately shut off pumps. Vent excess pressure. Inspect and unblock downstream line. Pressure relief valve RV 3–1 will open for pressures exceeding 300 bar.

(Table E- 11 continues)

Guide Word	Deviation	Cause	Consequences	Action
High	Pressure drop (DP)	Blockage in column packing	Possible rupture of DP cell diaphragms	Alarm on DP 3–1 will shut off the system. Shut off all pumps and inspect the column for blockages
↑	↑	Blockage in DP sensor capillaries	↑	↑
↑	Liquid level	Infrequent draining	Liquid build–up in column	Liquid level alarm L 3–1 will sound on the control box and turn off the system after a set time. Periodically drain liquid holdup from the column

Table E- 12: HAZOP table for Pressure Control Valve CV 4-1.

Process unit:		CV 4–1 [Pressure Control Valve]		
Intention:		Keeps column at operating pressure		
Standard operation:		Up to 200 °C and 300 bar		
Guide Word	**Deviation**	**Cause**	**Consequences**	**Action**
No	Flow	Control valve CV 4–1 faulty	No overhead product flow from column. Possible pressure build–up.	Check control valve CV 4–1 and control panel settings
↑	↑	Electric failure	↑	Check current to control panel and solenoid
↑	↑	Blocked line up– or downstream	↑	Inspect and unblock line
↑	↑	Blocked column	↑	Inspect and unblock column
↑	↑	Valve NV 3–9 or NV 3–10 closed	↑	Check valve NV 3–9 or NV 3–10
↑	↑	Valve NV 4–1 closed	↑	Check valve NV 4–1
Low	Flow (Liquid)	Valve NV 3–9 or NV 3–10 not fully open	Throttling of product flow. Possible precipitation of overhead product	Check valve NV 3–9 or NV 3–10
↑	↑	Valve NV 4–1 not fully open	↑	Check valve NV 4–1
↑	↑	Control valve CV 4–1 setpoint too high	Throttling of product flow	Check control valve CV 4–1 and control panel settings
↑	Temperature	Wrong setting or faulty heater H2	Possible product precipitation causing blockage in the line.	Alarm on T 4–1 will indicate a temperature outside range. Check heater H2. Alarm on heater will indicate a faulty heater
↑	↑	Temperature valves TV 11 and/or 12 closed or partially closed	↑	Alarm on T 4–1 will indicate a temperature outside range. Check temperature valves TV 11 and/or 12

(Table E- 12 continues)

Guide Word	Deviation	Cause	Consequences	Action
Low	Pressure	Control valve CV 4–1 setpoint too low	Incorrect column operating pressure. Possible precipitation of overhead	Check control valve CV 4–1 and control panel settings
High	Flow (Liquid)	Control valve CV 4–1 setpoint too low	Low pressure in column. High pressure in separator. Possible precipitation of overhead product.	Check control valve CV 4–1 and control panel settings
↑	↑	Utility air closed or pressure too low	↑	Check utility air valve UV 3. Check utility air pressure
↑	Temperature	Wrong setting on heater H2	Thermal degradation or burning of product.	Alarm on T 4–1 will indicate a temperature outside range. Check heater H2
↑	Pressure	Control valve CV 4–1 setpoint too high	No/low overhead product flow from column. Possible pressure build–up.	Check control valve CV 4–1 and control panel settings. Pressure relief valve RV 3–1 will open at high pressures
↑	↑	Electric failure	↑	Alarm on P 4–1 may shut off system. Otherwise immediately shut off pumps. Check current to control panel and solenoid. Pressure relief valve RV 3–1 will open at high pressures. For extreme cases burst disk BD 4–1 will burst.

Table E- 13: HAZOP table for Overhead Product Separator V 4-1.

Process unit:	V 4–1 [Overhead Product Separator]			
Intention:	Separates liquid and gaseous solvent product			
Standard operation:	Up to 200 °C and 100 bar			
Guide Word	**Deviation**	**Cause**	**Consequences**	**Action**
No	Flow (Total)	Faulty control valve CV 4–1	No overhead product flow to separator	Check control valve CV 4–1 and control panel settings
↑	↑	Valve NV 4–1 closed	↑	Check valve NV 4–1
↑	↑	Blockage in upstream line	↑	Inspect and unblock upstream line
↑	Flow (Liquid)	Separator pressure too high	No liquid precipitation.	See separator high pressure.
↑	↑	Filter and/or demister incorrectly installed	Liquid flow trapped in clogged demister.	Depressurise system, open separator and inspect and/or clean filter–demister setup
↑	Flow (Solvent)	Blockage in downstream line	↑	Inspect and unblock downstream line
↑	↑	Valve NV 4–4 closed	↑	Check valve NV 4–4
↑	↑	Filter and/or demister clogged	No solvent recycle.	Depressurise system, open separator and inspect and/or clean filter–demister setup
Low	Flow (Liquid)	Filter and/or demister incorrectly installed	Liquid flow trapped in clogged demister.	Depressurise system, open separator and inspect and/or clean filter–demister setup
↑	↑	Separator pressure too high	Poor liquid precipitation.	See separator high pressure.
↑	Flow (Solvent)	Filter and/or demister clogged	↑	Depressurise system, open separator and inspect and/or clean filter–demister setup

(Table E- 13 continues)

Guide Word	Deviation	Cause	Consequences	Action
Low	Temperature	Wrong setting or faulty heater H2	Incorrect separator temperature	Alarm on T 4–2 will indicate a temperature outside range. Check heater H2. Alarm on heater will indicate a faulty heater
↑	↑	Temperature valve TV 13 closed or partially closed	↑	Alarm on T 4–2 will indicate a temperature outside range. Check temperature valve TV 13
↑	Pressure	Control valve CV 4–1 faulty or at too low setpoint	Incorrect separator pressure	Check control valve CV 4–1 and control panel setpoint
↑	↑	Valve NV 4–2, NV 4–3 and/or RV 4–1 open	↑	Check valves NV 4–2, NV 4–3 and RV 4–1
High	Temperature	Wrong setting on heater H2	Incorrect separator temperature. Thermal degradation or burning of product.	Alarm on T 4–2 will indicate a temperature outside range. Check heater H2
↑	Pressure	Control valve CV 4–1 faulty or setpoint too low	Pressure build–up. Bad precipitation of product.	Alarm on P 4–2 may go off and turn the system off after a set time. Check control valve CV 4–1 and control panel settings. Alarm on P 4–2 will go off and turn the system off after a set time. Pressure relief valve RV 4–1 will open for extreme cases.
↑	↑	Valve NV 4–4 not fully open	↑	Alarm on P 4–2 may go off and turn the system off after a set time. Check valve NV 4–4. Pressure relief valve RV 4–1 will open for extreme cases.

Appendix F: Detailed Experimental Method

As the pilot plant was designed and built with future use in mind the following procedure is structured in such a way to be easily accessible for future users and not only applicable to this study. First the procedure for new users is established, followed by a typical start-up, operating and shutdown procedure in point wise fashion. The instructions for hydrodynamic experiments, developed for this work, is also covered in this section. All valves and pieces of equipment referred to here can be viewed in Figures 3–3 to 3–8 in Section 4.2.

F.1 For First-time Users

Before a new operator operates the pilot plant for the first time, it is advised that they adhere to the following procedure. This will ensure that the pilot plant is kept in good working order and that the new user operates it safely.

1. Get familiarized with the pilot plant manual, especially the relevant safety documents and the process description.

2. Do a cursory check for leaks, especially heating oil, or obvious damage to the system.

3. Check if any pressure remains in the system from previous experiments. If pressure is present, vent in a safe manner.

4. Check the system maintenance schedule if any maintenance is due and perform as instructed in the pilot plant manual.

5. Check both the gearbox and hydraulic oil levels of the pumps and the heating oil level of the oil heaters, H1 and H2, and top up if required. The appropriate oils are recorded in the pilot plant manual.

6. Check if the system is clean, especially the feed vessel, V 1-1, and the separator vessel, V 4-1.

7. Check what kind of packing is in the column(s) and if the packing is clean. If needed, change the packing type as described in the pilot plant manual. If the packing is changed a pressure test of the column is advised, followed by an air scouring as described in step 10.

8. Check if the optical level sensors and sapphire cones are clean.

9. If in any of the above three steps the pilot plant is found in an unsatisfactory state, determine an appropriate cleaning solvent such as ethanol or warm soapy water. Avoid acetone as it can damage seals in the system. The chosen solvent is loaded into the feed vessel, V 1-1 and separator, V 4-1, and circulated by turning on the liquid and solvent feed pumps, P 1-1, P 1-2 and P 2-1. Manual cleaning of the separator is required. If required, the oil heaters, H1 and H2, can be turned on to aid in cleaning.

10. If the system is cleaned with a solvent, ensure the system is purged of the solvent by washing with pure water and/or scouring with compressed air. Scouring by air is done by

connecting the compressed air hose to valve NV 1-1 for the liquid feed lines, NV 3-3 and NV 3-4 for Column 3-1 and 3-2 respectively, and NV 4-2 or NV 4-3 for the solvent section.

11. If any connections are loosened during cleaning or inspection, ensure that they are tightly fastened afterwards.

12. Ensure the cooling fans and radiators of the pump motors, heaters and refrigeration condenser are clean for optimal operation. Compressed air can be used to remove any loose dirt.

13. If a leak on the system is suspected, see the plant manual section for leak trouble-shooting.

F.2 Start-up Procedure

The following steps should be performed when preparing to start a run on the pilot plant:

1. Switch on the main power supply to the pilot plant.

2. Ensure that a flash drive with the correct file system (FAT 32) and sufficient free space is plugged into the HMI system to record the logging data.

3. Check that the compressed air valve, UV 3, is open and delivers sufficient pressure. To check the air supply, open the utility nozzle air valve, UV 2 and observe if sufficient pressure is present.

4. Ensure that valves BV 1-1, BV 1-2 and NV 1-1 are closed.

5. Place the liquid feed into the feed vessel, V 4-1. If the component is prone to evaporation or hygroscopic, add the lid and screw down tightly.

6. Switch on heaters H1 and H2 and input the desired temperatures into the heaters, noting that the actual temperature is about 15°C below the heater set point for heater H1 and 5- 10°C above for heater H2. Allow for sufficient time for the system to reach thermal equilibrium. It is advised that this is done at least 2 hours in advance for lower temperatures (up to 60°C) and the previous day for higher temperatures (up to 200°C), to allow for sufficient heating time.

7. Switch on the cooling water at the cooling water mains and open valves UV 1 and UV 2 to allow for cooling water flow.

8. Switch on the refrigeration unit on the refrigeration control panel. Ensure that the set temperatures are correct for the selected solvent as specified in Table F-1. Allow for 15-30 minutes for the refrigeration to reach operating temperatures.

Table F-1: Refrigerator temperature and controller set values for different supercritical fluids.

	Condensor		Pump Suction	
Supercritical Fluid	Temperature	Controller Setting	Temperature	Controller Setting
CO_2	5 - 22 °C	10	-2 - 9 °C	10
Ethane	5 - 22 °C	10	-2 - 9 °C	10
Propane	15 - 30 °C	20	10 - 20 °C	20
n-Butane	25 - 40 °C	25	20 - 30 °C	25

The system is now ready for the loading and priming of the solvent section. This is done by doing the following:

9. Turn on the extractor fans in the lab in case of a gas leak. Ensure no ignition sources are present when using a flammable solvent such as ethane or propane.

10. Before loading solvent ensure that the following valves are fully closed: NV 1-1 through 1-7, NV 2-2, NV 2-4, NV 3-1 through 3-10, NV 4-1 through 4-4.

11. Check that the following valves are fully open: NV 2-2, NV 2-3, and NV 2-5.

12. If needed adjust the regulator valve, SV 2-1, in the solvent recycle loop. For start-up it is advised that the valve is fully open.

13. When connecting a new cylinder, first close valve NV 2-1 and connect the cylinder. Open the cylinder main valve, followed by opening valve NV 2-1. It is advised to open the valve slowly, especially when operating with carbon dioxide, to avoid ice forming in the lines.

14. If a new solvent is used, the system should be vented. This is done in the following manner:

    14.1 Open valves NV 2-2, NV 3-1, NV 3-2, NV 3-9, NV 3-10, NV 4-1 and override CV 4-1 on the separator section on the HMI (see Appendix D: Figure D-6). If the valve is overridden, the button will turn green.

    14.2 Briefly open valves NV 2-4, NV 3-3, NV 3-4, NV 4-2 and NV 4-3.

    14.3 After this, reclose the valves NV 2-2, NV 3-1, NV 3-2, NV 3-9, NV 3-10 and NV 4-1 and return control to CV 4-1 by pressing the override button again. If the override function is off, the button will appear yellow.

15. Ensure the stroke length for the solvent feed pump, P 2-1, is set to 10 mm.

16. To load solvent, select the 'Start-up' sequence on gas feed section on the HMI (see Appendix D: Figure D- 4). This will bypass certain alarms and allow the P 2-1 to be turned on to start circulating the solvent.

17. Turn on Solvent pump P 2-1 on the HMI in the gas feed section as soon as sufficient liquid is in the solvent tank.

18. Monitor the gas feed pressure on local pressure indicator PI 3-1. If the pressure increases significantly above the gas bottle pressure, switch off the pump immediately.

19. Wait for the solvent to reach an acceptable liquid level, as can be observed in the level gauge. A level of three quarters is recommended for standard operation. Close NV 2-1 to ensure an accurate mass flow reading.

20. Slowly open Valves NV 4-1, NV 4-4 and either valves NV 3-1 and V3-9 for operating column C 3-1 or NV 3-2 and NV 3-10 for column C 3-2.

21. Set the pressure set point for the control valve SV 2-1 to a value just above the currently circulating solvent pressure as read from PI 3-1. This is done in the separator section on the HMI (see Appendix D: Figure D- 6).

22. Slowly close valve NV 2-3 to close the solvent recycle loop.

23. Increase the set point for the control valve stepwise by about 10 bar to the selected column pressure, allowing for the system to adjust for a few minutes between steps. See Table F- 2 for recommended minimum values for a few supercritical solvents.

Table F- 2: Solvent critical pressure and suggested minimum operating pressure.

Supercritical Colvent	Critical Pressure (bar)	Sugested Minimum Pressure (bar)
CO_2	73.8	±90
Propane	42.5	±60
Ethylene	50.6	±70
n–Butane	38.0	±60

24. Allow the system to run for five minutes to allow the gas to circulate.

25. The solvent feed pump, P 2-1, can now be adjusted to the appropriate setting by manually turning the solvent feed pump dial. Fine tuning of the flow rate with respect to the mas flow sensor is advised. Remember to lock the pump safety lever at the appropriate setting.

26. If the control valve response is unsatisfactory or too big, the momentary pressure drop caused by control valve CV 4-1 can be choked by partially closing NV 4-1. This provides back pressure which keeps the pressure drop from fluctuating wildly. Note that if this is applied, the column pressure has to be monitored carefully to avoid pressure build-up.

27. If a solvent flow rate that is very low, or less than the pump minimum is required, the recycle loop can be kept open and throttled to provide a smaller net flow:

    27.1 First allow the pilot plant to reach steady state at an intermediate solvent flow value. It is very important to ensure a constant flow for this operation mode.

    27.2 Note the current mass flow value.

    27.3 Turn on the 'Bypass'-option on the gas feed section of the HMI (see Appendix D: Figure D- 4). Input the current average mass flow into the box as prompted. The calculated mass flow value should now appear as a separate block below the current mass flow and should currently be around zero.

    27.4 Now open valve NV 2-3 and adjust the regulator valve SV 2-1 until an appropriate calculated mass flow is obtained. Note that the calculated mass flow in this option is inaccurate and should be used with discretion. Do not adjust the pump flow rate or any throttling valves, as this will render the calculated value meaningless.

28. Ensure that no major pressure build-up occurs beyond the extraction pressure. This is done by monitoring PIC 4-1 on the HMI or the local pressure indicators PI 3-1 and PI 4-1. If this occurs, immediately vent the column at valves NV 3-3 and NV 3-4 for columns C 3-1 and C 3-2 respectively.

29. Optimize the column pressure by changing the set point if required. If the drop in pressure from the opening and closing of the control valve CV 4-1 is too large, back pressure can be applied by partially closing NV 4-1.

The system is now ready to start an extraction or a hydrodynamic experiment:

F.3 Standard Extraction Operation

30. Ensure that the liquid feed level is high enough in the feed vessel, V 1-1, and that the vessel is open to the atmosphere to prevent a vacuum from forming. In the case of fluids that prove difficult to pump or are prone to evaporation, pressurised air or nitrogen pressure can be applied to the feed vessel.

31. Open valve BV 1-1 and NV 1-2 to use the small capacity feed pump, P 1-1, or valve BV 1-2 and NV 1-3 for the large capacity feed pump, P1-2. For flows between 0 and 2 ℓ the small pump is recommended, while for flows between 2 and 8 ℓ, using the larger pump is advised.

32. Open the relevant valves to select the feed position for the chosen column:

    32.1 Column C 3-1:

        32.1.1 Top feed: Valves NV 1-7 and NV 3-6.

        32.1.2 Middle feed: Valves NV 1-6 and NV 3-8.

    32.2 Column C 3-2:

        32.2.1 Top feed: Valves NV 1-7 and NV 3-5.

        32.2.2 Middle feed: Valves NV 1-6 and NV 3-7.

33. In order to allow pressure to be read in the liquid feed pressure gauge, and in some cases allow for liquid flow, open valve NV 1-5.

34. Set the relevant liquid feed pump to the required setting. The required setting can be obtained by consulting the pump calibration curves in Appendix C, C2.

35. Turn on the chosen feed pump in the liquid feed section of the HMI (see Appendix D: Figure D- 3). If hydrodynamic investigations are to be done delay this step.

36. For extended, runs monitor the level in feed vessel V 1- 1 and top up as needed. If the feed is to be heated, add in small amounts or preheat the liquid before adding it to the vessel.

37. Periodically decant and measure the column bottoms to avoid build-up. Column C 3-2 has a level sensor that will warn of build-up. It is advised that column C 3-1 is timed and periodically drained with respect to the liquid feed rate.

38. Periodically decant and measure the built up liquid from the separator, V 4-1, by opening valve NV 4-2. The separator has a big volume and typically only needs emptying at the end of a run. In the case of the separator becoming full a level sensor will warn the operator.

39. Periodically check the liquid solvent level in solvent feed tank V 2-1 to ensure the system does not run dry.

F.4 Hydrodynamic Experiments

These instructions are only relevant when performing hydrodynamic experiments, and as such they do not form part of the general instructions. The numbering in this section does not follow on the general operating instructions and is treated as a separate entity. It is assumed that all the steps up to this point have been followed in the preceding start-up and operating procedure sets.

The following procedure is for the measurement of hydrodynamic data, except for the static hold-up which is explained separately in a sub-section.

1. Turn the solvent feed rate to the first supercritical phase flow rate required.

2. Ensure the column bottoms and separator are empty of any liquids.

3. Allow the system time to reach equilibrium. Equilibrium is determined by monitoring the pressure drop over the column and the liquid solvent mass flow rate. As soon as the respective trends stop fluctuating for an extended period equilibrium is assumed. This can take up to an hour.

4. Check the liquid feed rate to ensure it is at the desired level. Turn on the pump while noting the starting time of the run.

5. Again monitor the pressure drop over the column to determine the new equilibrium state with the liquid flow included.

6. Periodically decant and weigh and/or measure the volume the column bottoms and overheads, as dictated by the liquid flow rate. This is done by opening NV 3-3 for column C 3-1, NV 3-4 for column C 3-2 for the bottoms and NV 4-2 for the overheads. Only slightly open valves and decant small amounts of liquid to avoid the draining of the liquid affecting the equilibrium significantly. Note that if the column floods overheads will drastically increase.

7. As soon as equilibrium is reached, note the current time on the HMI system. The system pressure drop, temperature and solvent flow rate can later be averaged from logged data at or around this time.

8. To measure liquid hold-up, the following procedure is used:

    8.1 After equilibrium is reached, drain all of the liquid from the bottom of the column.

    8.2 Once all the liquid has drained stop the liquid feed pump and open NV 2-3 to bypass the solvent immediately.

    8.3 Allow time for the liquid in the packing to drain out. This process is dependent on the packing geometry and the viscosity of the fluid and can take a significant amount of time. Keep completely draining the hold-up at set intervals until the liquid captured becomes negligible. Weigh and/or measure the volume of the hold-up.

    8.4 Briefly close NV 2-3 to pump solvent to the column to evacuate any remaining liquid hold-up from the solvent feed pipe that may have accumulated. Allow for some time to settle and drain the column again.

9. Raise the liquid feed rate to a higher level and repeat steps 4 to 8.

10. As soon as the liquid overheads show sharp increases, it can be assumed that the column has flooded. Level sensor L 3-2 should also be indicating a liquid level. Flooding concludes the measurement at a specific liquid flow rate. It is, however, advised to measure a few further data points to confirm that flooding has occurred and provide a complete picture of a system.

11. To measure at a different solvent flow rate, adjust the solvent feed pump and repeat the above procedure.

All the required readings such as temperature, pressure, solvent flow rate and pressure drop is recorded onto the flash drive, by the HMI system. After an experimental set, the flash drive must be removed safely, to avoid data loss, by using the main screen (see Appendix D: Figure D-1), whereafter the data can be recovered using a computer. The recovered data can be compared to the time values noted during the experiment to identify the exact data required.

F 4.1 Static Liquid Hold-up

Static liquid hold-up, as defined in Section 2.2.6, has to be measured with dry packing before any liquid is allowed to wet the packing surface. The following procedure is followed to measure static hold-up:

1. Follow the start- up and operating procedure instruction sets up to point 35. This puts the system at the state just before the liquid feed pumps are turned on.

2. Turn the large liquid feed pump P 1-2 up to a pump stroke length of 11.85 mm. This provides a known flow rate of 6 ℓ/h. To ensure accuracy the flow rate can be checked by opening NV 1-4 and measuring the volumetric flow.

3. Ensure the pump feeds to the top of the selected column.

4. Turn off the solvent feed pump and ensure the control valve and/or NV 4-1 is closed at the desired column pressure. This is to avoid the liquid leaving through column top.

5. Prepare a stopwatch to take a timed reading.

6. Turn the large liquid feed pump on and start the stopwatch simultaneously.

7. Allow the pump to run for exactly two minutes on the stopwatch before turning it off. This allows 200 ml of liquid to enter the system. The piping to the columns retains some of the liquid, with ≈14.9 ml retained before C 3-1 and ≈15.0 ml before C3-2, with the rest entering the column.

8. Allow time for the liquid to drain to the column bottom.

9. After enough time has elapsed, drain the liquid into a measuring cylinder opening NV 3-3 for column C 3-1 and NV 3-4 for column C 3-2 in short, small bursts and note the volume.

10. Subtract the drained volume and the retained liquid from the total liquid fed (200 ml) to determine the static liquid hold-up.

F.5 Shutdown

Once an experimental run is complete, the following procedure should be followed:

40. Turn off the appropriate liquid feed pump on the HMI liquid feed section (see Appendix D: Figure D- 3).

41. Close the valves used to feed the liquid to the column:

    41.1 Column C 3-1:

        41.1.1 Top feed: Valve NV 3-6.

        41.1.2 Middle Feed: Valve NV 3-8.

    41.2 Column C 3-2:

        41.2.1 Top feed: Valve NV 3-5.

        41.2.2 Middle Feed: Valve NV 3-7.

42. Allow the solvent to circulate for a further 20 minutes, especially in the case of an extraction run. This removes any remaining light product in the column and top product line. Continue draining column bottoms and overheads as needed.

43. Turn off the solvent pump, P 2-1, in the gas feed section of the HMI (see Appendix D: Figure D- 4).

44. Relieve any remaining pressure in the liquid feed line by draining the line at valve NV 1-4.

45. Drain any remaining liquid feed in the feed tank, V 1-1, by opening valve NV 1-1

46. If the solvent is to be reused, it can be stored in the system overnight. The following measures should be taken:

    46.1 Reduce the column set pressure in 10 bar steps to the solvent tank pressure.

    46.2 Close valve NV 2-5 to keep the liquid solvent from leaving the buffer tank, V 2-1. The check valve CHV 2-3 will prevent flow into the separator. It is not critical, but advised to close the following valves to isolate equipment and decrease the effect of possible leaks: NV 2-2, NV 2-3, NV 3- 1, NV 3-2, NV 3-9, NV 3-10, NV 4-1 and NV 4-3.

46.3 Vent the column used by opening valve NV 3-3 for column C 3-1 and valve NV 3-4 for column C 3-2 and catching any remaining liquid. If no more liquid exits the column, the system can be fully depressurised if desired.

46.4 Vent the separator by opening valve NV 4-3, again catching any remaining liquid. If no more liquid exits the separator, the system can be fully depressurised if desired.

46.5 The solvent is now safe to store until the next run.

47. If the solvent is not to be stored, follow steps 46.1, 46.3 and 46.4, after which the solvent buffer tank, V 2-1, can be depressurised by opening valve NV 2-4.

48. Turn off the oil heaters H1 and H2

49. After allowing for a further 10 minutes turn off the refrigeration system, R1.

50. Turn off the control panel and the pilot plant mains.

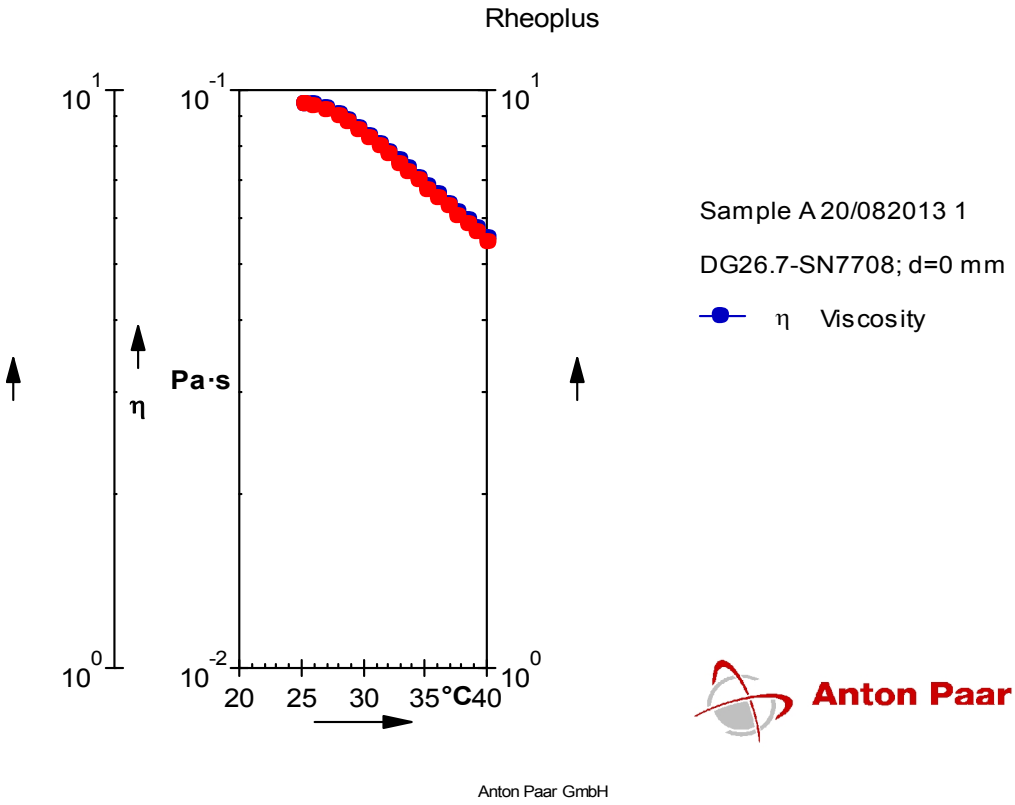
The pilot plant is now safe and ready for the next experimental run, except when the same liquid feed is used. If this is not the case, see steps 8-10 in the instructions for first time users, in Appendix F, F.1, or consult the pilot plant manual for the appropriate cleaning procedure. It is also advised that the solvent be replaced if liquids are changed, as some residual dissolved liquid may be present in the solvent.

Appendix G: Experimental Data

Various parts of data gathered are represented in this section. The order of appearance is as follows:

In the raw data graphs the pressure drop is shown in the unusual units of daPa or decapascal in order to comfortably fit on the axis with the pressure drop.

G.1 PEG 400 Viscosity



Meas. Pts.	Shear Rate	Temperature	Shear Stress	Viscosity	Speed	Torque
	[1/s]	[°C]	[Pa]	[mPa·s]	[1/min]	[µNm]
1	100	25.4	9.48	94.8	32.3	867
2	100	25.4	9.47	94.7	32.3	867
3	100	26.1	9.43	94.3	32.3	863
4	100	27.2	9.29	92.9	32.3	849
5	100	28.1	9.07	90.7	32.3	830
6	100	28.9	8.84	88.4	32.3	809
7	100	29.7	8.59	85.9	32.3	786
8	100	30.6	8.34	83.4	32.3	763
9	100	31.4	8.08	80.8	32.3	739
10	100	32.2	7.82	78.2	32.3	715
11	100	33	7.56	75.6	32.3	692
12	100	33.8	7.31	73.1	32.3	669
13	100	34.6	7.06	70.6	32.3	646
14	100	35.4	6.83	68.3	32.3	624
15	100	36.2	6.6	66	32.3	603
16	100	37	6.37	63.7	32.3	583
17	100	37.8	6.16	61.6	32.3	563
18	100	38.6	5.95	59.5	32.3	545
19	100	39.4	5.75	57.5	32.3	526
20	100	40.1	5.56	55.6	32.3	509

G.2 Experimental Results and Calculated Values

Table G- 1: Summary of experimental data.

Gas Flow Rate (kg/min)	Gas Density (kg/m^3)	Gas Viscosity (Pa.s)	Liquid Mass Flow Rate (kg/min)	Solvent /Liquid Feed Ratio	Average Column Temp (°C)	Average Column Pressure (bar)	Run Duration (mins)	Measured Column Bottoms (g/min)	Measured Column Tops (g/min)	Measured Liquid Holdup (g)	Column Top Liquid Alarm	Flooding	Dry Pressure Drop (Pa/m)	Pressure Drop per unit length (Pa/m)
0.453	716.02	5.829E-05	0.038	12.08	40.00	119.4	24.83	27.75	1.78	115.42	N	N		361.3
0.488	716.06	5.843E-05	0.056	8.69	39.99	119.7	45.98	28.58	0.95	222.83	N	N		464.0
0.462	728.54	5.997E-05	0.075	6.19	38.88	119.6	36.12	53.80	1.36	410.19	N	N	212.7	921.3
0.474	728.23	5.992E-05	0.093	5.07	38.91	119.6	49.83	38.57	12.33	1260.11	Y	Y		3468.7
0.442	712.72	5.786E-05	0.112	3.95	40.24	119.2	33.83	55.13	12.19	1065.18	Y	Y		3491.3
0.562	709.13	5.740E-05	0.038	14.97	40.43	118.7	42.42	26.52	1.55	154.86	N	N		468.7
0.564	704.6	5.682E-05	0.056	10.05	40.80	118.6	31.20	40.99	1.40	284.77	N	N		1001.3
0.593	713.96	5.803E-05	0.075	7.93	40.16	119.3	43.00	31.45	1.62	651.36	N	N	299.3	1632.4
0.578	718.2	5.858E-05	0.093	6.19	39.88	119.7	29.33	29.13	19.31	1193.77	Y	Y		3394.0
0.562	712.81	5.788E-05	0.112	5.02	40.40	119.8	23.83	22.95	22.32	1218.89	Y	Y		3539.3
0.642	722.61	5.917E-05	0.038	17.10	39.60	120.2	29.00	22.09	2.06	173.68	N	N		654.0
0.670	725.83	5.961E-05	0.056	11.93	39.58	121.3	22.17	26.50	1.73	279.1	N	N		1423.3
0.672	721.3	5.901E-05	0.065	10.27	39.96	121.1	52.83	38.67	1.72	630.41	N	N		3057.3
0.667	724.45	5.942E-05	0.075	8.92	39.40	120.1	40.67	45.35	2.44	670.16	Y	N	450.7	3279.3
0.670	726.38	5.968E-05	0.084	7.97	39.19	120.0	26.50	26.52	9.76	1110.69	Y	Y		3076.0
0.656	721.23	5.899E-05	0.093	7.03	39.73	120.2	28.05	26.13	15.54	1129.93	Y	Y		3170.0
0.656	733.06	6.060E-05	0.112	5.86	38.95	121.6	20.17	23.83	19.77	1101.91	Y	Y		3299.3
0.768	706.01	5.700E-05	0.038	20.46	40.87	119.3	39.33	12.57	2.03	168.12	N	N		1082.7
0.778	733.19	6.059E-05	0.056	13.86	38.10	118.3	34.75	17.51	3.02	284.27	N	N		1116.0
0.760	705.36	5.692E-05	0.075	10.17	40.90	119.2	37.45	33.95	2.77	750.54	Y	N	546.0	2340.7
0.760	708.59	5.733E-05	0.093	8.14	40.45	118.6	37.17	20.65	19.23	1074.10	Y	Y		3111.3
0.796	706.6	5.707E-05	0.112	7.11	40.68	118.8	39.83	21.99	35.67	1052.86	Y	Y		3214.7
0.860	726.08	5.964E-05	0.038	22.9	39.40	120.7	50.88	16.75	2.43	158.1	N	N		1412.7
0.858	697.58	5.595E-05	0.056	15.3	41.80	120.0	43.83	30.26	1.97	291.3	N	N		1192.7
0.855	713.28	5.795E-05	0.075	11.4	40.60	120.7	68.43	39.49	2.43	953.4	Y	N	799.3	3339.3
0.899	738.31	6.132E-05	0.093	9.6	38.10	120.3	31.53	21.55	20.04	1083.2	Y	Y		3492.7
0.870	707.79	5.725E-05	0.112	7.8	41.40	121.8	28.47	19.57	23.83	1013.5	Y	Y		3246.0

Table G- 2: Values calculated from raw data in Table G- 1.

Gaseous Superficial Velocity (m/s) x10³	Liquid Superficial Velocity (m/s) x10³	Gas Capacity Factor (m/s)(kg/m³)$^{0.5}$ x10³	Liquid Holdup (m³/m³)	Re_G	ψ	dP_o/H (Pa)	Dissolved Frac
9.306	0.499	12.626	0.0614	68.58	1.5354	16.61	0.0039
10.011	0.747	13.583	0.1185	73.60	1.5125	18.93	0.0019
9.327	0.994	12.975	0.2182	67.99	1.5383	17.01	0.0029
9.557	1.241	13.287	0.6703	69.69	1.5300	17.75	flooded
9.123	1.489	12.297	0.5666	67.42	1.5411	15.95	flooded
11.648	0.499	15.589	0.0824	86.35	1.4664	24.61	0.0027
11.765	0.747	15.607	0.1515	87.55	1.4627	24.88	0.0025
12.206	0.994	16.494	0.3465	90.12	1.4552	27.00	0.0027
11.831	1.241	16.121	0.6351	87.02	1.4643	25.67	flooded
11.583	1.489	15.615	0.6484	85.59	1.4687	24.50	flooded
13.056	0.499	17.948	0.0924	95.67	1.4404	30.95	0.0032
13.565	0.747	18.769	0.1485	99.10	1.4321	33.36	0.0026
13.691	0.870	18.772	0.3354	100.42	1.4290	33.70	0.0026
13.530	0.994	18.668	0.3565	98.98	1.4324	33.14	0.0036
13.555	1.118	18.775	0.5909	99.00	1.4323	33.34	0.0144
13.367	1.241	18.324	0.6011	98.06	1.4346	32.24	0.0231
13.151	1.489	18.462	0.5862	95.45	1.4410	31.86	0.0293
15.986	0.499	21.265	0.0894	118.80	1.3936	43.86	0.0026
15.601	0.747	21.908	0.1512	113.27	1.4030	43.67	0.0039
15.843	0.994	21.048	0.3993	117.80	1.3952	43.09	0.0036
15.764	1.241	21.076	0.5714	116.91	1.3967	42.90	flooded
16.548	1.489	22.039	0.5601	122.93	1.3871	46.82	flooded
17.406	0.499	24.095	0.0841	127.14	1.3809	52.99	0.0028
18.076	0.747	23.652	0.1550	135.22	1.3701	54.47	0.0023
17.624	0.994	23.783	0.5072	130.16	1.3767	53.20	0.0028
17.898	1.241	25.396	0.5762	129.30	1.3779	56.84	flooded
18.064	1.489	24.114	0.5391	133.99	1.3717	56.04	flooded

G.3 Solvent Flow Rate ~0.47 Results

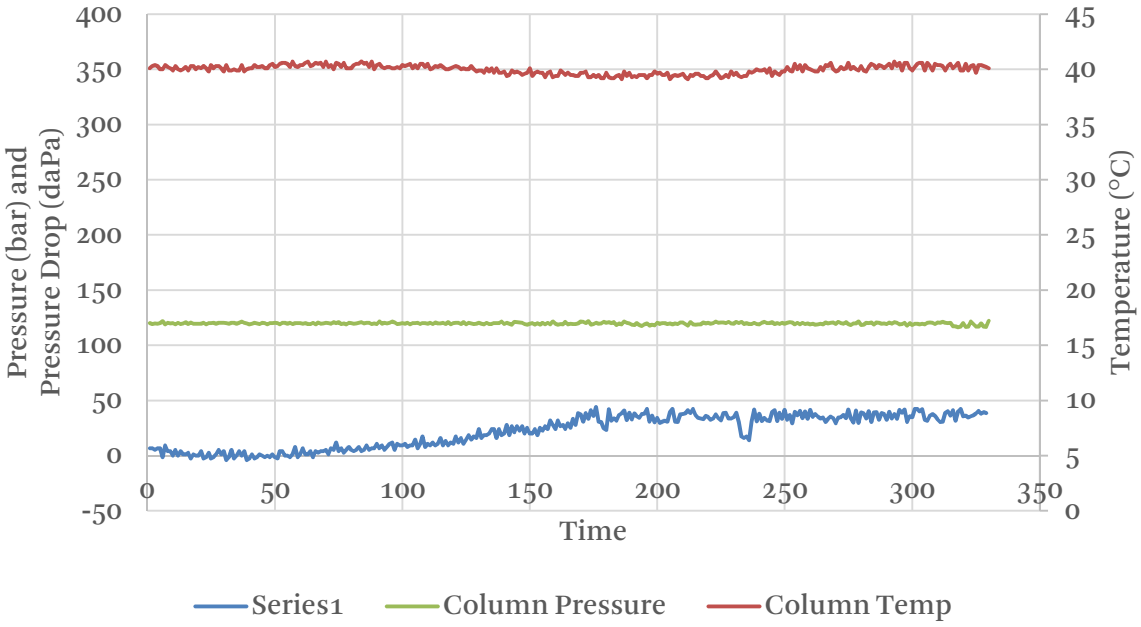


Figure G- 1: Pilot plant results for 0.038 kg/min liquid flow at ~0.47 kg/min gas flow rate.

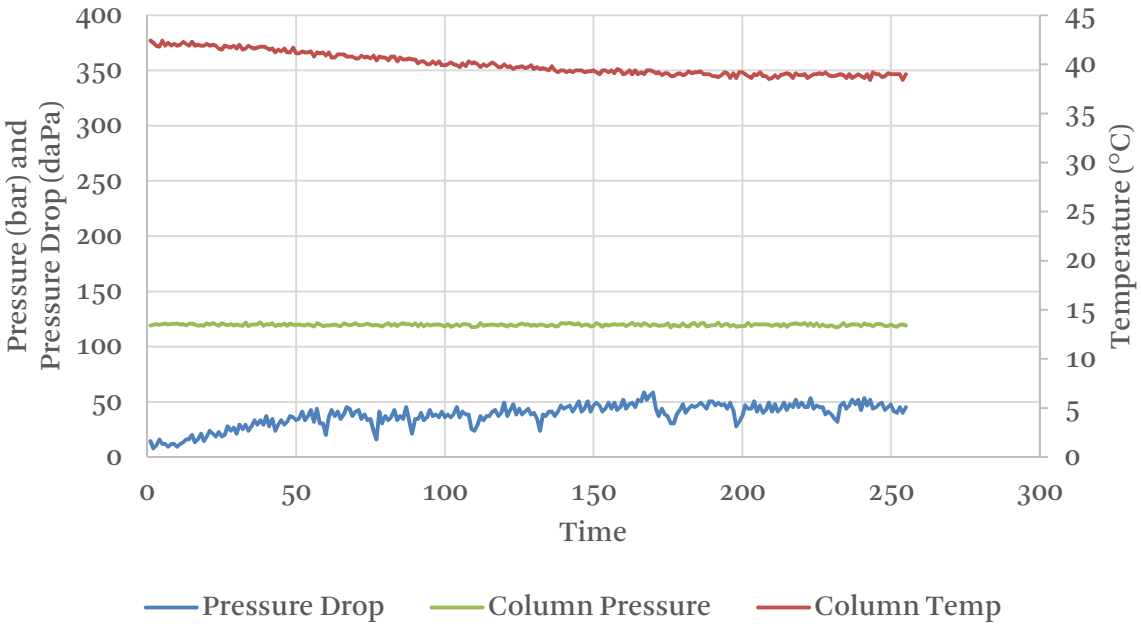


Figure G- 2: Pilot plant results for 0.056 kg/min liquid flow at ~0.47 kg/min gas flow rate.

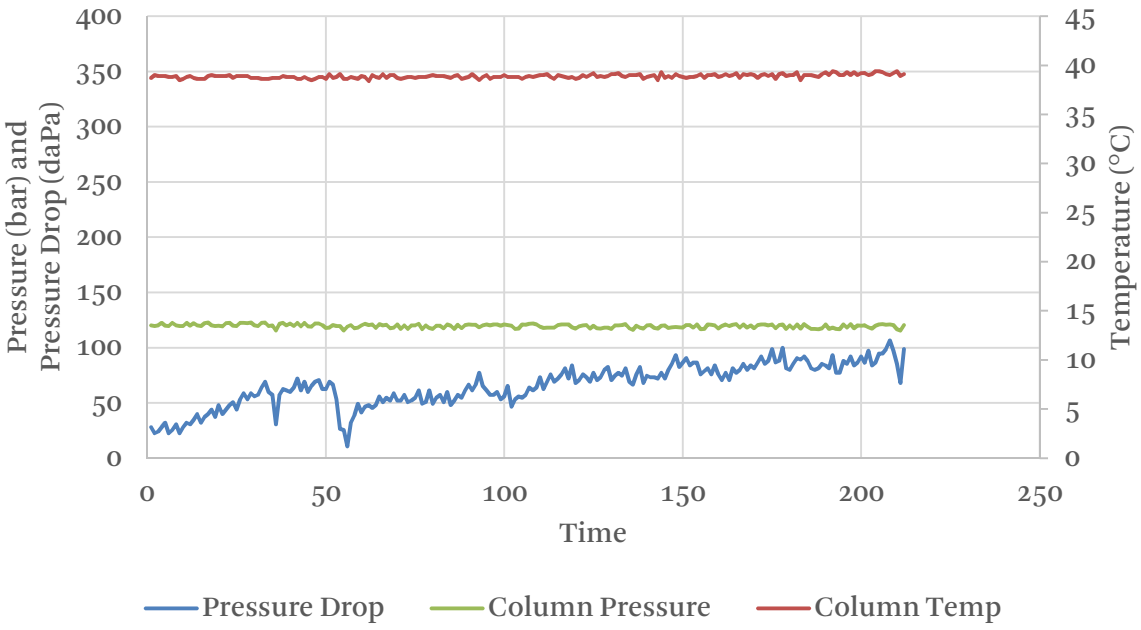


Figure G- 3: Pilot plant results for 0.075 kg/min liquid flow at ~0.47 kg/min gas flow rate.

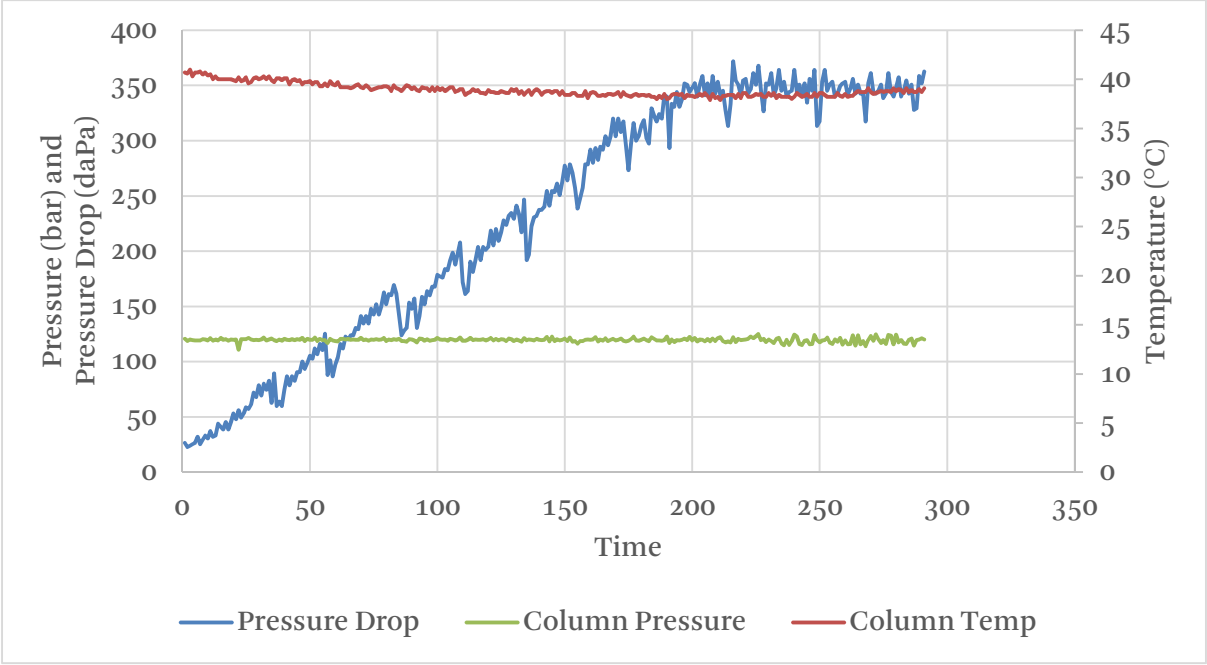


Figure G- 4: Pilot plant results for 0.093 kg/min liquid flow at ~0.47 kg/min gas flow rate.

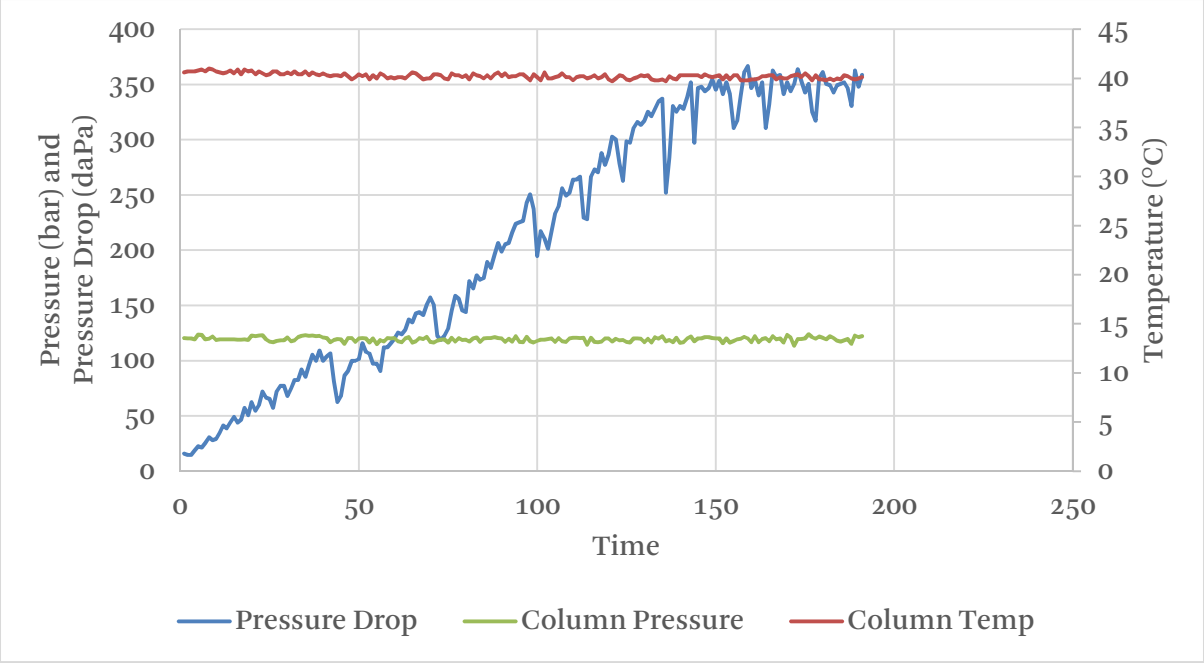


Figure G- 5: Pilot plant results for 0.112 kg/min liquid flow at ~0.47 kg/min gas flow rate.

G.4 Solvent Flow Rate ~0.57 Results

Due to a file being corrupted the first, third and last trends of the 0.57 kg/min gas flow rate was unfortunately lost. Fortunately the pressure drop, column pressure and temperature averages were already determined and written down on a paper backup copy. It is assumed these trends will fall between that of the prior and following solvent flow rates.

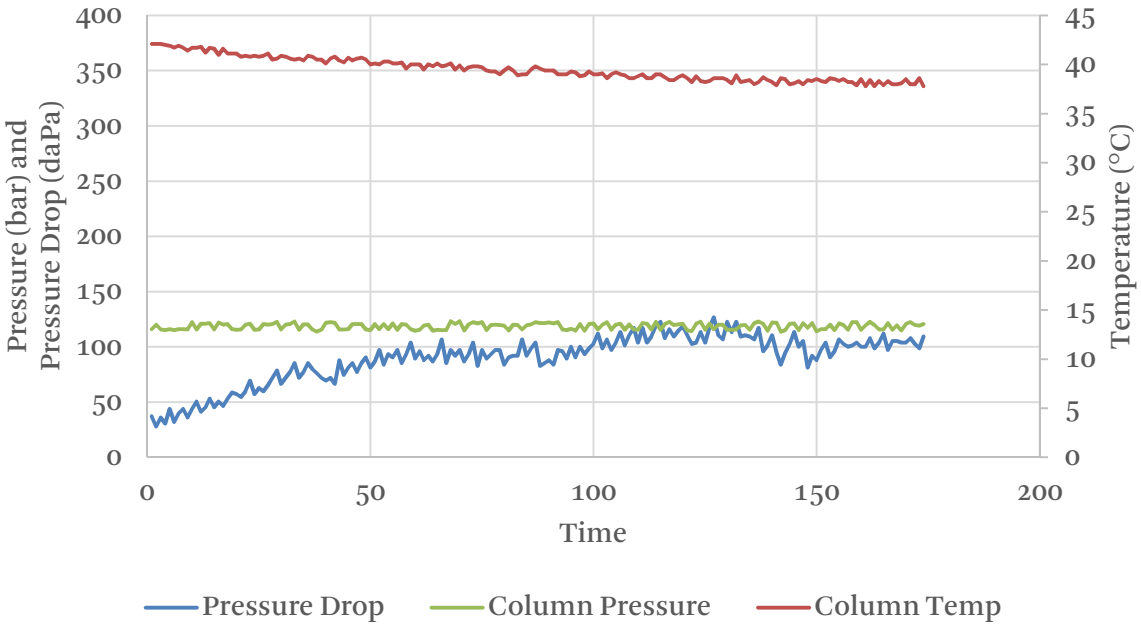


Figure G- 6: Pilot plant results for 0.056 kg/min liquid flow at ~0.57 kg/min gas flow rate.

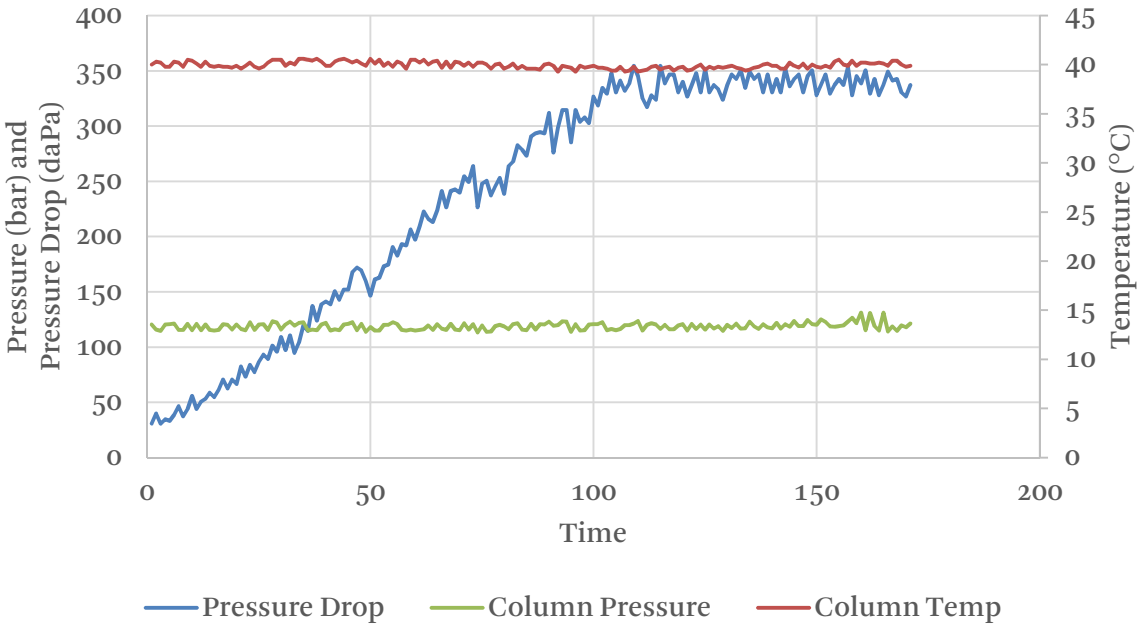


Figure G- 7: Pilot plant results for 0.093 kg/min liquid flow at ~0.57 kg/min gas flow rate.

G.5 Solvent Flow Rate ~0.67 Results

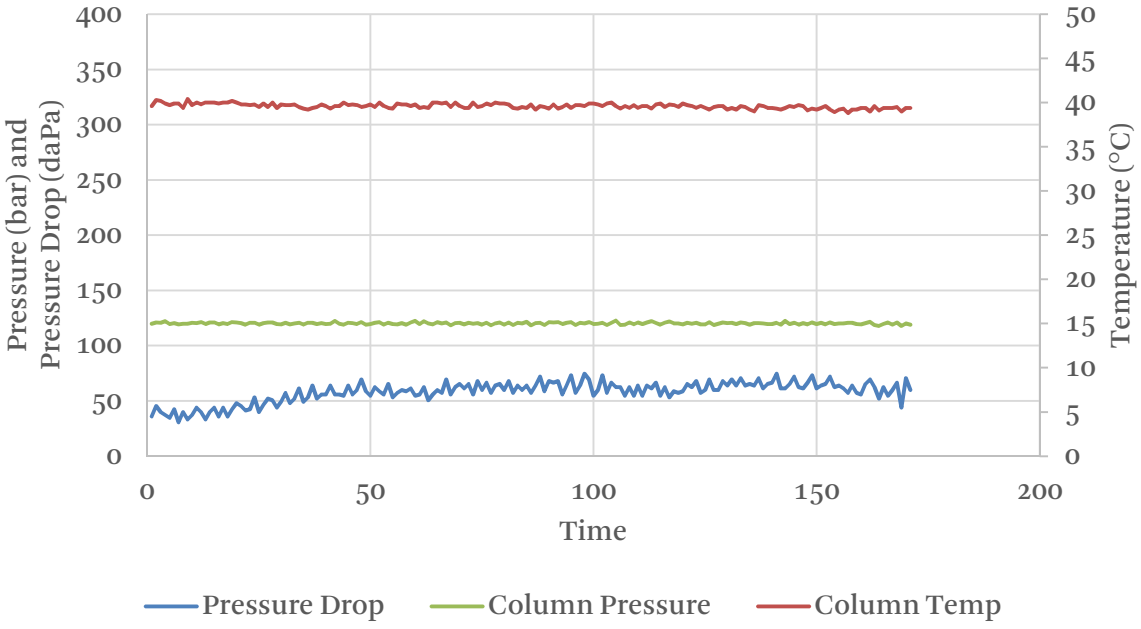


Figure G- 8: Pilot plant results for 0.038 kg/min liquid flow at ~0.67 kg/min gas flow rate.

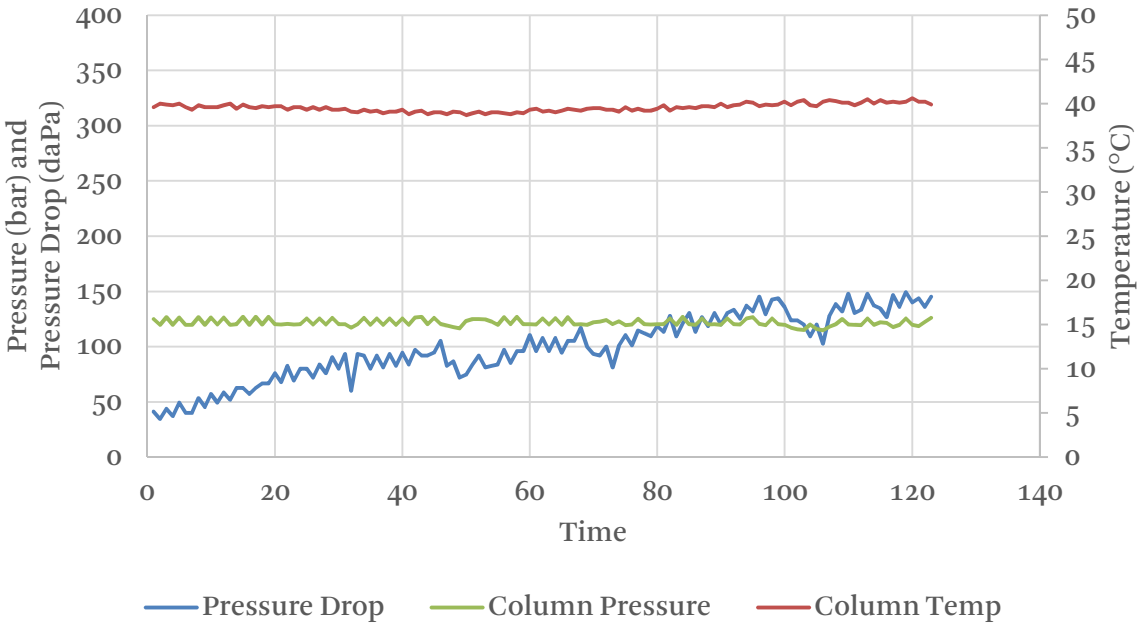


Figure G- 9: Pilot plant results for 0.056 kg/min liquid flow at ~0.67 kg/min gas flow rate.

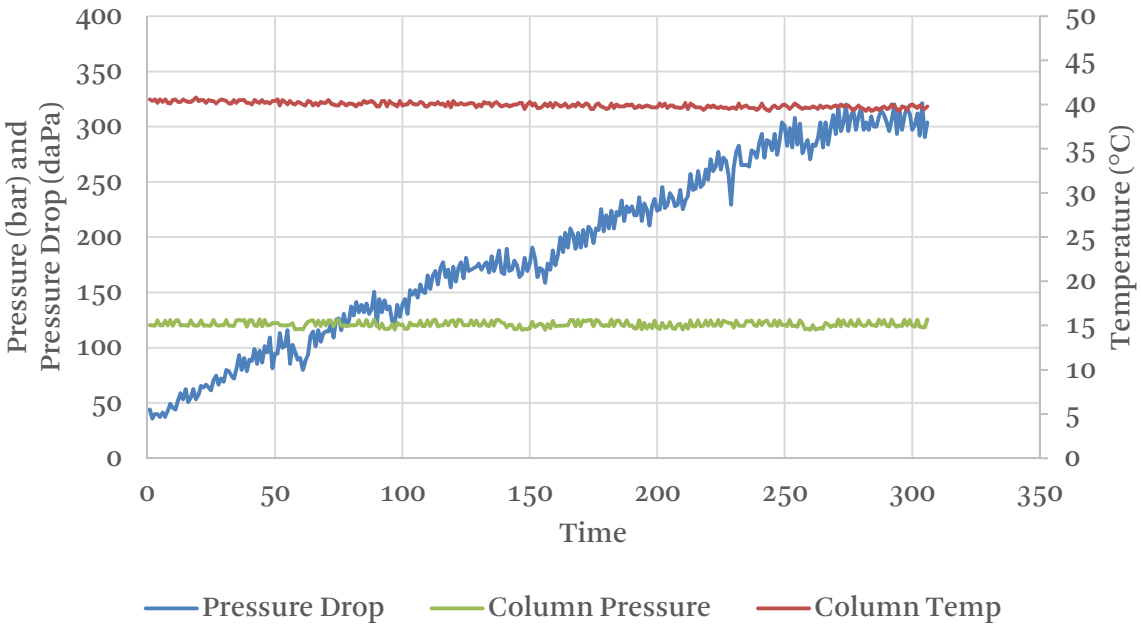


Figure G- 10: Pilot plant results for 0.065 kg/min liquid flow at ~0.67 kg/min gas flow rate.

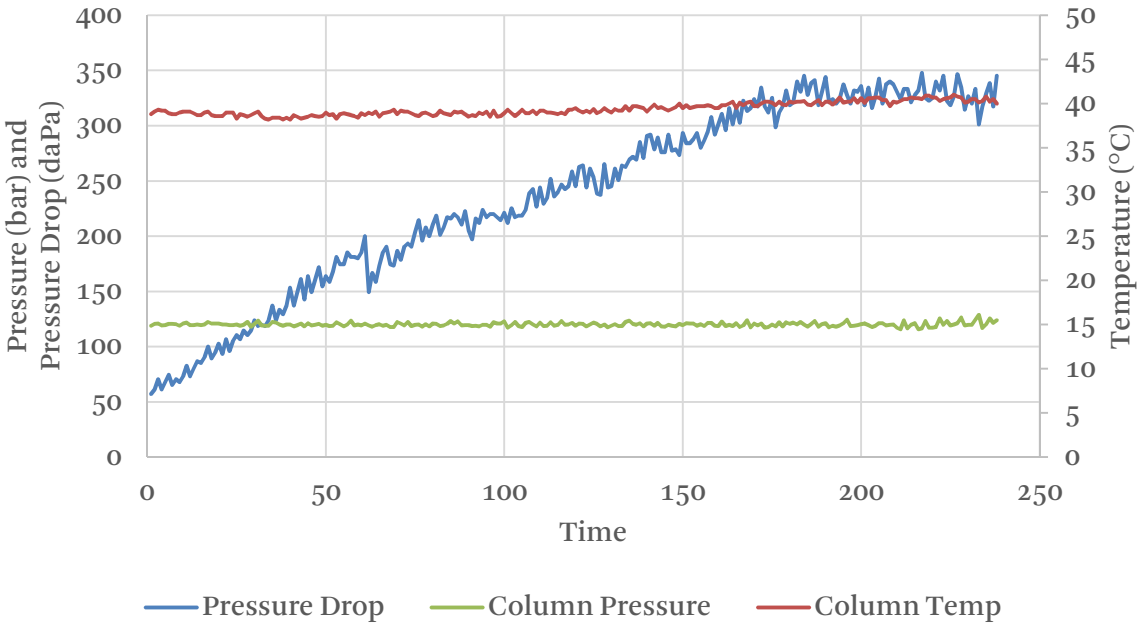


Figure G- 11: Pilot plant results for 0.075 kg/min liquid flow at ~0.67 kg/min gas flow rate.

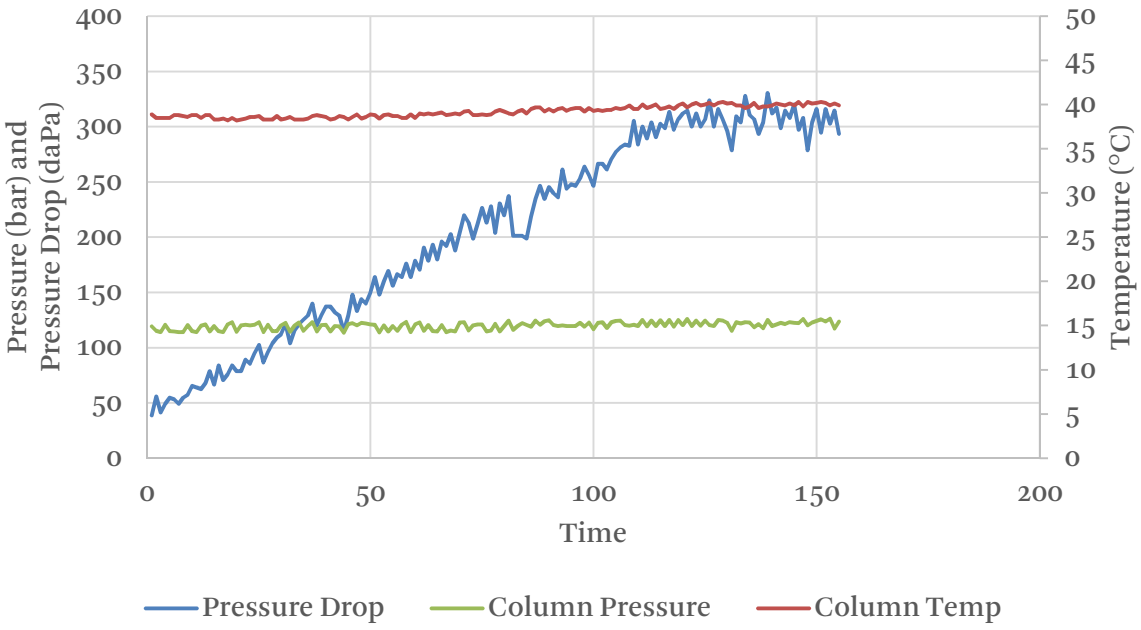


Figure G- 12: Pilot plant results for 0.084 kg/min liquid flow at ~0.67 kg/min gas flow rate.

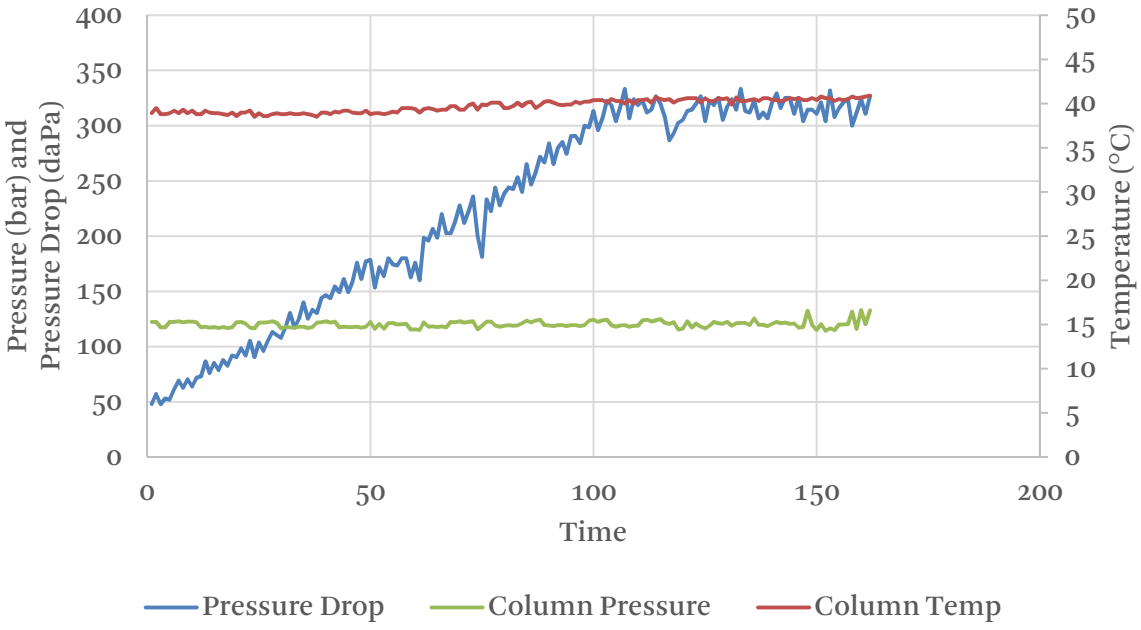


Figure G- 13: Pilot plant results for 0.093 kg/min liquid flow at ~0.67 kg/min gas flow rate.

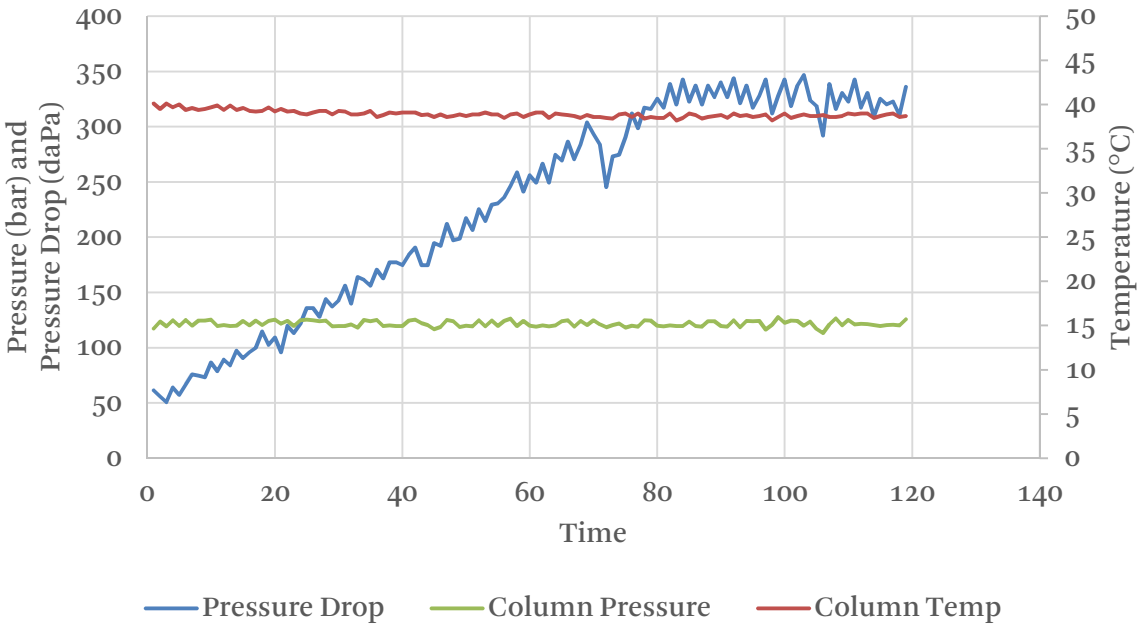


Figure G- 14: Pilot plant results for 0.112 kg/min liquid flow at ~0.67 kg/min gas flow rate.

G.6 Solvent Flow Rate ~0.77 Results

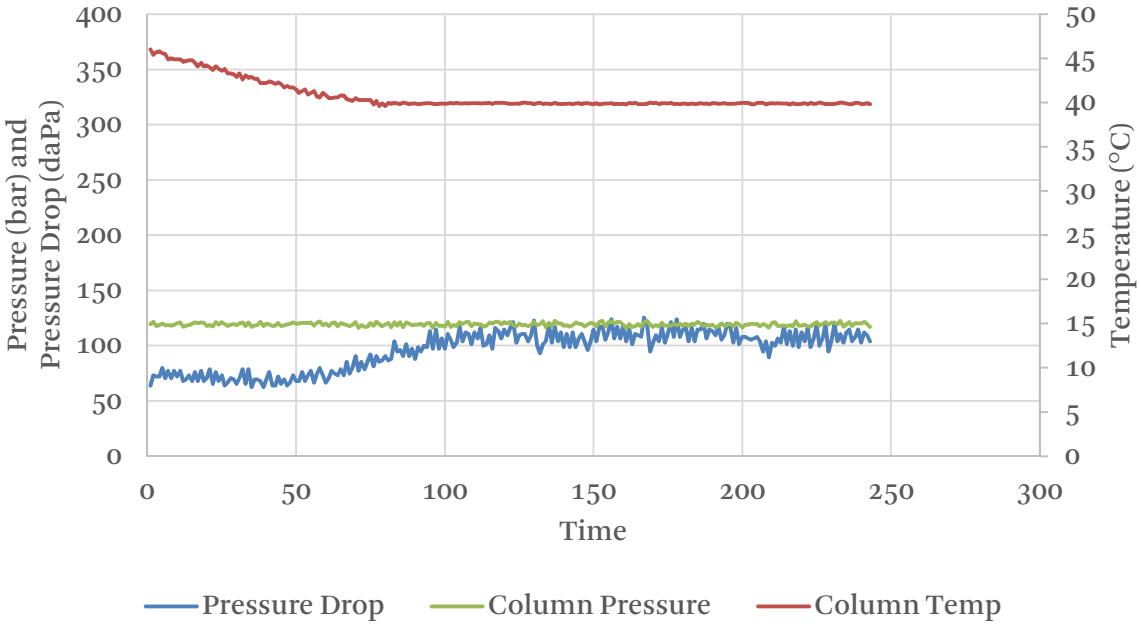


Figure G- 15: Pilot plant results for 0.038 kg/min liquid flow at ~0.77 kg/min gas flow rate.

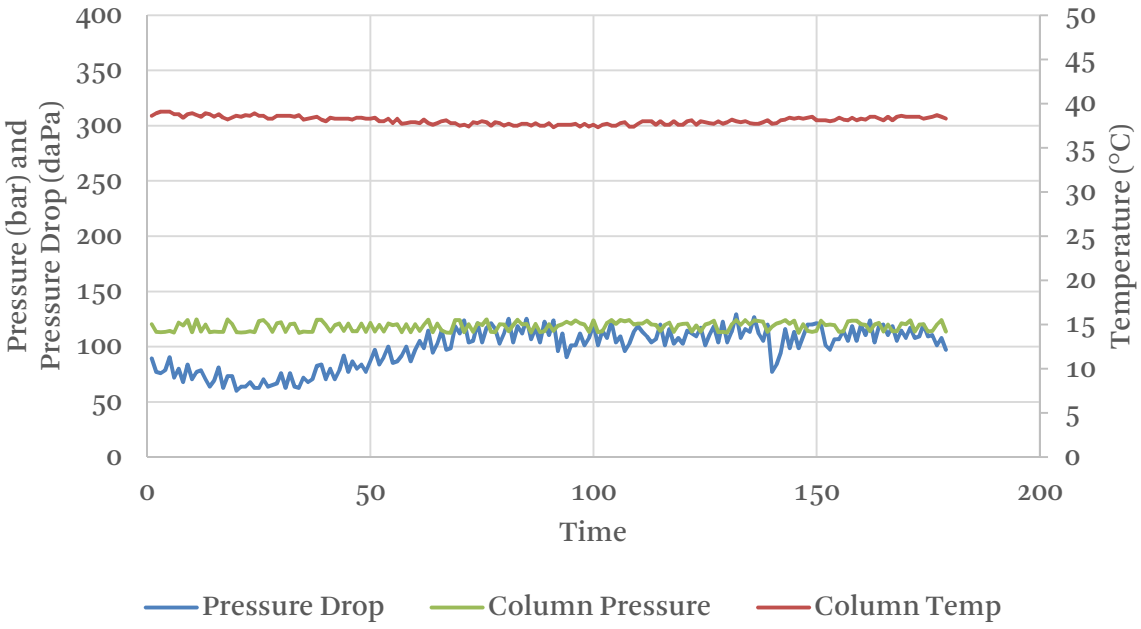


Figure G- 16: Pilot plant results for 0.056 kg/min liquid flow at ~0.77 kg/min gas flow rate.

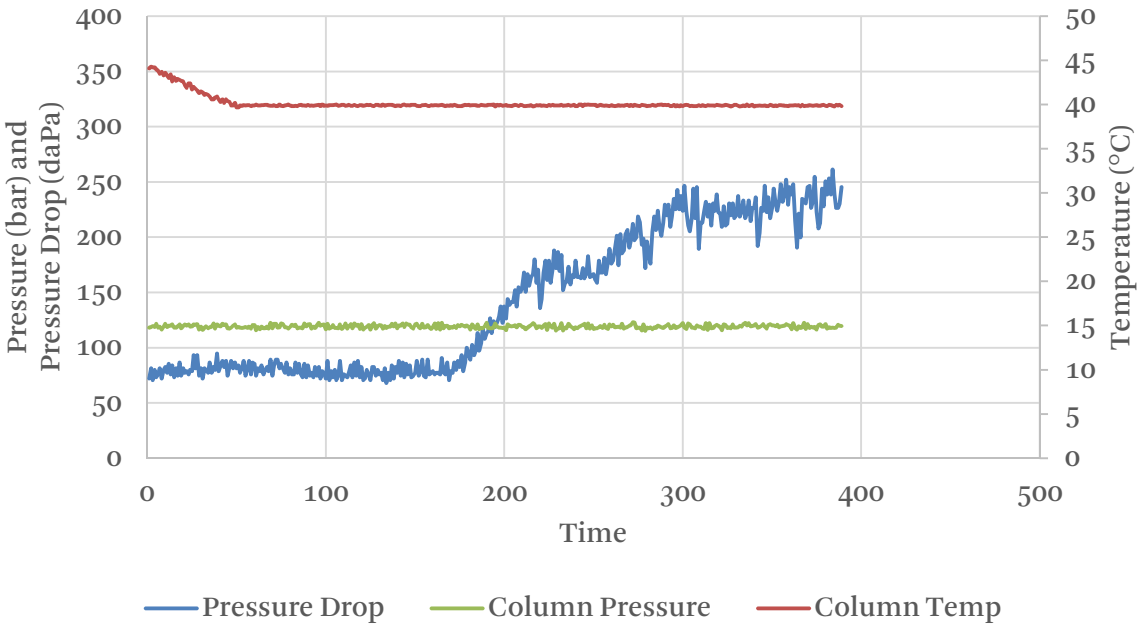


Figure G- 17: Pilot plant results for 0.075 kg/min liquid flow at ~0.77 kg/min gas flow rate.

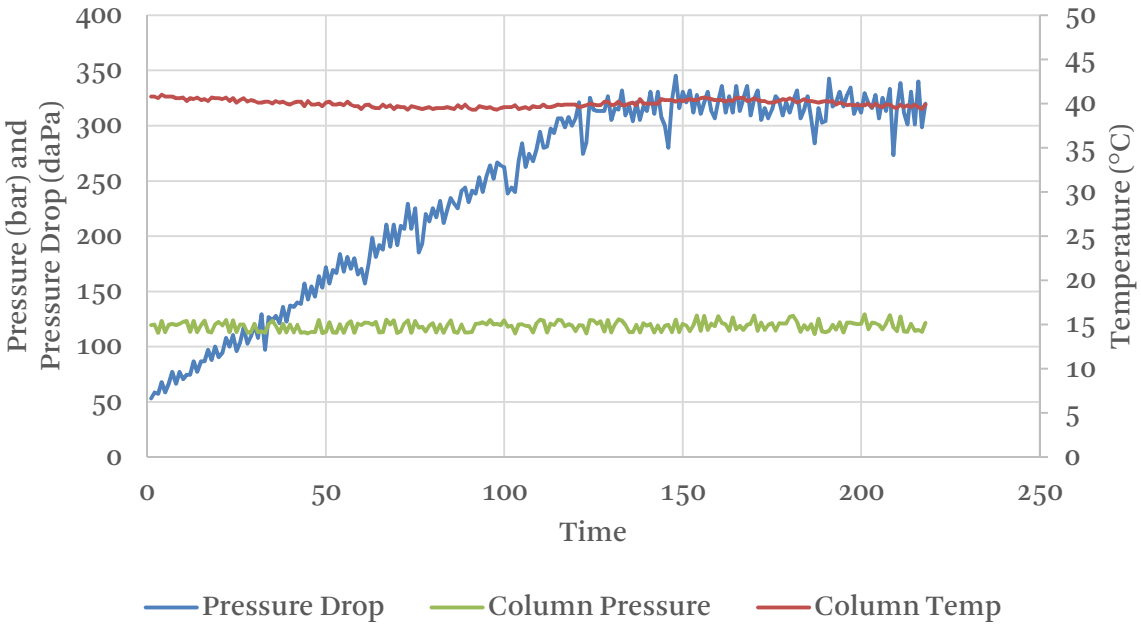


Figure G- 18: Pilot plant results for 0.093 kg/min liquid flow at ~0.77 kg/min gas flow rate.

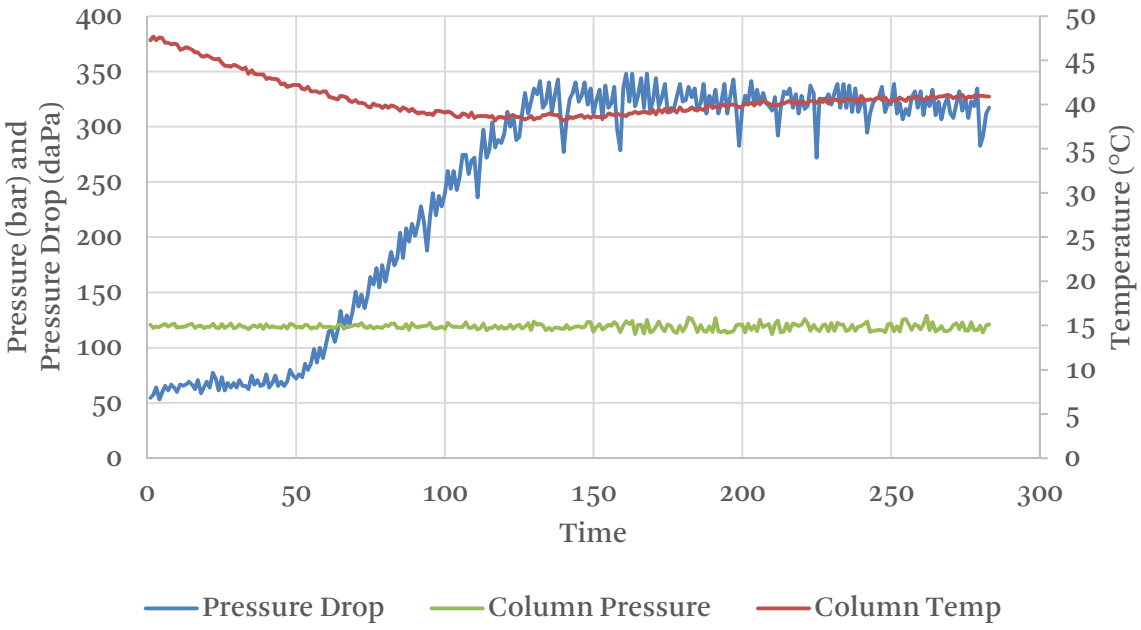


Figure G- 19: Pilot plant results for 0.112 kg/min liquid flow at ~0.77 kg/min gas flow rate.

G.7 Solvent Flow Rate ~0.87 Results

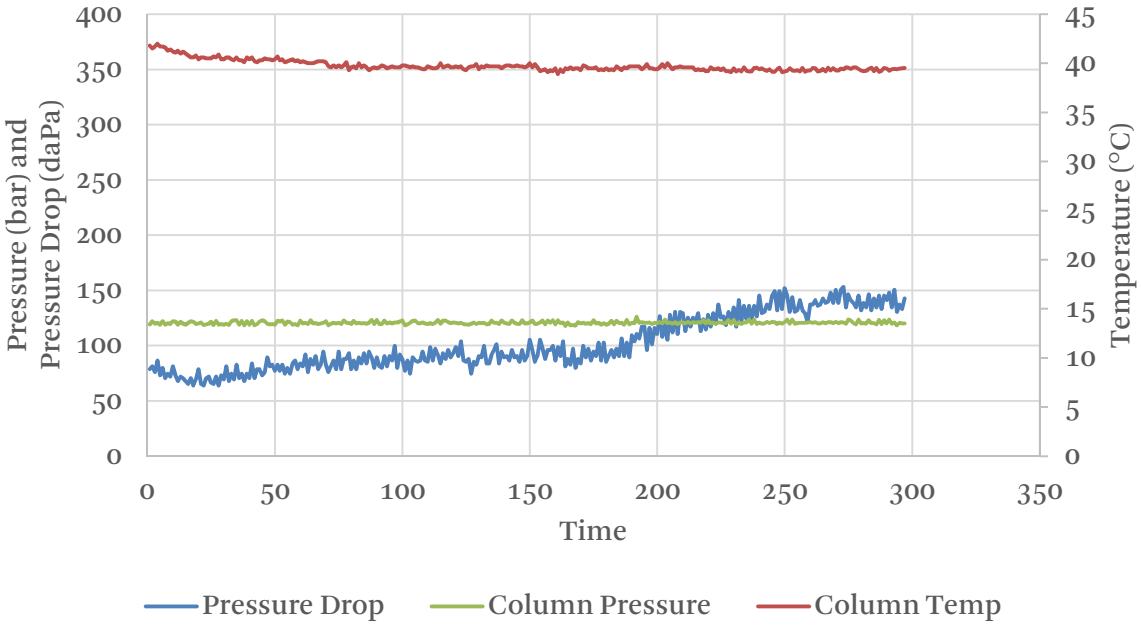


Figure G- 20: Pilot plant results for 0.038 kg/min liquid flow at ~0.87 kg/min gas flow rate.

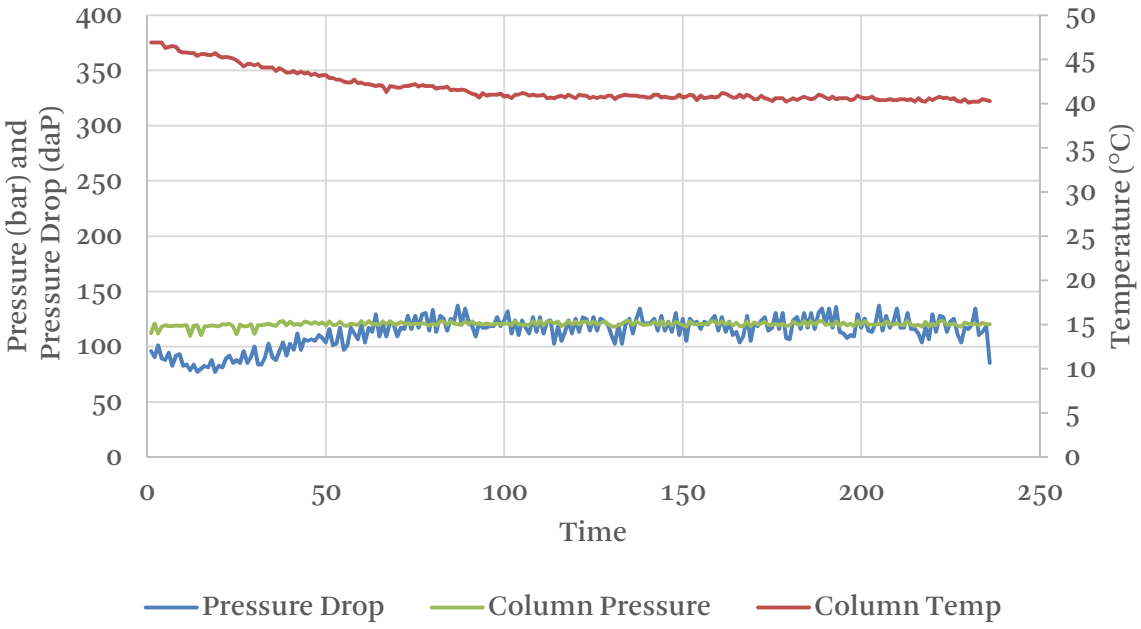


Figure G- 21: Pilot plant results for 0.056 kg/min liquid flow at ~0.87 kg/min gas flow rate.

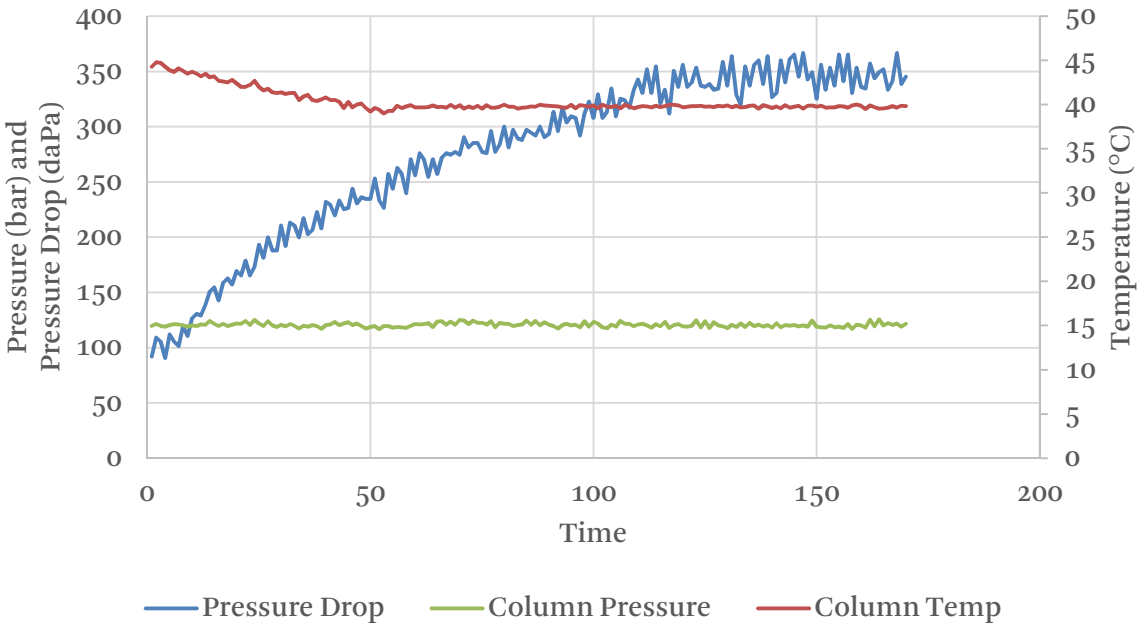


Figure G- 22: Pilot plant results for 0.075 kg/min liquid flow at ~0.87 kg/min gas flow rate.

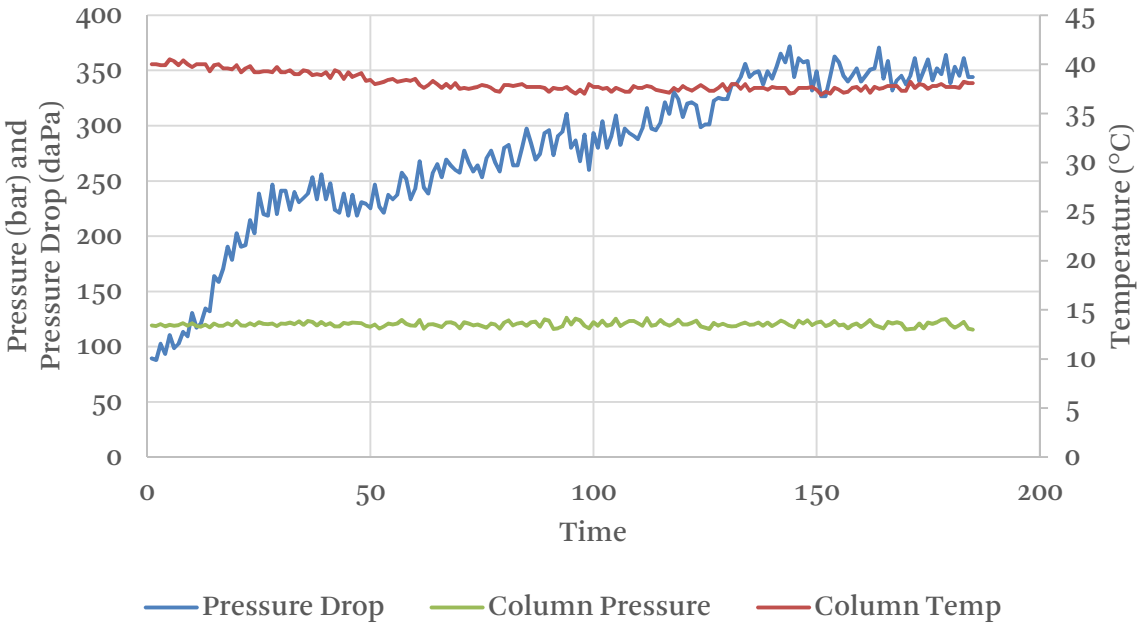


Figure G- 23: Pilot plant results for 0.093 kg/min liquid flow at ~0.87 kg/min gas flow rate.

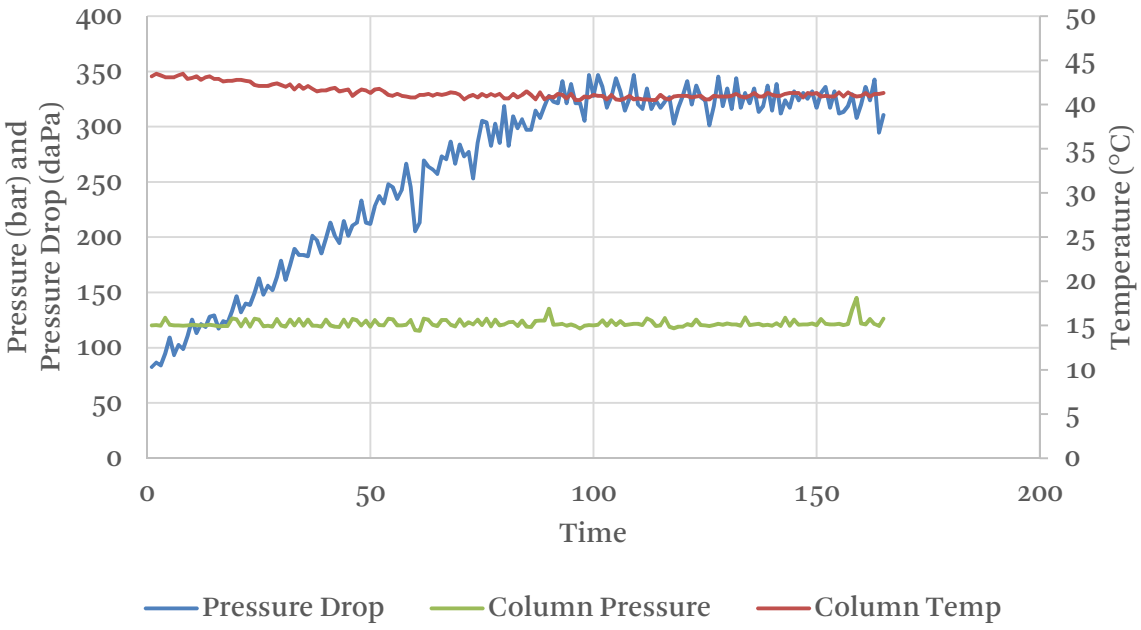


Figure G- 24: Pilot plant results for 0.112 kg/min liquid flow at ~0.87 kg/min gas flow rate.

"Logic is a wonderful thing, but doesn't always beat actual thought."

— Terry Pratchett